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# Polyol-polymer mixture for long-term latent heat storage

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**Abstract of master's thesis**

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## Abstract

In this work, novel phase change material (PCM) based on polyol-polymer mixture was developed for long-term thermal energy storage purposes, which is especially relevant for cold-climate regions, such as Nordic countries due to high heat demand in winter time. Unlike to the currently used sensible heat storages, supercooling PCMs provide large energy density in smaller volume without the need for proper insulation due to the absence of heat losses over the storage period. The overview of thermal energy storage technologies is presented in the theoretical section with the emphasis on cold-crystallization mechanism, which is based on the supercooling effect of the material and allows to significantly prolong the storage period. This thesis has been conducted under the umbrella of Heatstock Project concentrating on developing reliable long-term heat storage materials.

The novel material consists of erythritol and mannitol mixture, improved by dispersing it in polyvinyl alcohol as a supporting polymer matrix. Due to the ability to vitrify and to cold-crystallize, the material is capable of storing the heat in supercooled state and controllably releasing it when the discharge is triggered by heat impulse. In the experimental section the optimal PCM composition is defined on the basis of its thermal behavior, analyzed by means of differential scanning calorimetry (DSC). The specific heat capacity measurement is performed to estimate the approximate triggering heat impulse and prove the PCM's feasibility for industrial applications. The storage and cycling stability were confirmed by bulk storage tests of 10 g samples and 50 consecutive DSC heating-cooling cycles. The PCM also demonstrated good thermal stability within operation temperature range (up to 150°C).

The results display promising perspectives of using polyol-polymer mixture as PCM for long-term thermal energy storage. The novel material demonstrates high latent heat of melting (198 J/g) and crystallization (129 J/g), as well as good cycling stability of melting and the ability to store heat up to 2 weeks at 0°C in bulk size. Moreover, the addition of PVA allows to prevent melted PCM's leakage from container by giving it form-stability. Therefore, novel polyol-polymer mixture has a potential for further developing in terms of upscaling and increasing the storage period.

**Keywords** long-term heat storage, phase change material, polyol-polymer mixture, supercooling, cold-crystallization

# Contents

# Symbols

| | | |
|---|---|---|
| $C_{ap}$ | [J/g K] | average specific heat between $T_i$ and $T_f$ |
| $C_p$ | [J/g K] | specific heat capacity |
| $C_{p,l}$ | [J/g K] | average specific heat in liquid phase |
| $C_{p,s}$ | [J/g K] | average specific heat in solid phase |
| m | [g] | mass of heat storage medium |
| Q | [J] | quantity of heat stored |
| $T_c$ | [°C] | crystallization temperature |
| $T_{cc}$ | [°C] | cold crystallization temperature |
| $T_f$ | [°C] | final temperature |
| $T_g$ | [°C] | glass transition temperature |
| $T_i$ | [°C] | initial temperature |
| $T_l$ | [°C] | temperature of PCM in liquid phase |
| $T_m$ | [°C] | melting temperature |
| $T_s$ | [°C] | temperature of PCM in solid phase |
| $T_{st}$ | [°C] | storage temperature |
| $\Delta H_{cc}$ | [J/g] | enthalpy of cold crystallization |
| $\Delta H_m$ | [J/g] | enthalpy of melting |
| $\Delta H_{tr}$ | [J/g] | triggering heat impulse |
| $\Delta T_{sc}$ | [°C] | supercooling degree |

# Abbreviations

| | |
|---|---|
| DSC | Differential scanning calorimetry |
| EG | Expanded graphite |
| ERY | Erythritol |
| GHG | Greenhouse gases |
| IEA | International Energy Agency |
| IPCC | Intergovernmental Panel on Climate Change |
| MAN | Mannitol |
| PAANa | Sodium polyacrylate |
| PCM | Phase change materials |
| PVA | Polyvinyl alcohol |
| SC | Sodium citrate |
| TES | Thermal energy storage |
| TGA | Thermogravimetric analysis |

# 1 Introduction

The global energy demand is constantly growing, and world's energy sector still significantly relies on fossil fuels, which increases the environmental burdens. Thus, to mitigate $CO_2$ emissions and prevent an irreversible climate change, the large-scale implementation of sustainable technologies and renewable energy production is needed (1).

However, the variable production profile of renewable energy sources, for instance, wind and solar power plants, becomes a serious obstacle for complete substitution of fossil-based energy sources. To combat this challenge, energy storage technologies are needed as a necessary component of sustainable energy systems. Among them, thermal energy storage (TES) is a promising solution, as they enable the efficient management and utilization of renewable energy. TES can be based on using latent heat, sensible heat or heat from thermo-chemical processes and include a wide range of materials, depending on the desired properties (2).

Long-term thermal energy storage becomes especially important in cold climate regions. Large fluctuations of outdoor temperature and solar irradiation create the need for efficient technology to balance the energy system. It would allow to save the heat (e.g. from solar power plants) during summertime, store it for several month and then release it in winter, when district heating is needed. The possible solution in these circumstances would be latent heat TES based on phase change materials (PCM). Unlike to the widely used sensible heat storages, that require huge volumes and proper insulation, PCM-based latent heat storages have significantly larger energy densities (3).

The overall working principle of PCM as a heat storage is based on its ability to absorb and release heat during melting and crystallization processes, respectively. The supercooling effect occurs when PCM is cooled below its equilibrium phase change temperature and remains in liquid state without crystallizing. It is usually undesired in TES, as solidification does not happen when expected. However, using supercooled PCM has a great potential for long-term heat storage, because in case of absence of spontaneous crystallization the heat may be stored for several month without heat losses. To release the latent heat when it's needed, the crystallization is triggered by e.g. heat impulse (4, 5). The main challenges that limit the usage of PCM for long-term TES applications are related to metastability of supercooled liquid (and therefore the possibility of undesirable spontaneous crystallization), effective heat transfer and triggering crystallization (3, 6).

To this end, this work is focused on development of the novel cold crystallizing phase change material for long-term TES within a framework of Heatstock Project. Existing thermal energy storage technologies are reviewed in the theoretical part of the thesis with an emphasis on supercooling PCM. Based on the prior studies investigation, the novel polyol-polymer mixture is prepared and analyzed. The experimental section includes optimizing mixture composition and studying its thermal behavior, storage and cycling stability. The results show that the novel material has a promising potential for further research and development to be used as PCM for long-term TES.

# 2 Theoretical background

## 2.1 Role of energy storage in power systems decarbonization

The problem of carbon lock-in and consequential climate change draws careful attention on a global stage. According to Intergovernmental Panel on Climate Change (IPCC), the connection between increasing greenhouse gases emissions (GHG, such as $CO_2$) and global climate change is undeniable, which leads to inevitable degradation of living conditions for the whole humanity. As it stated in the global Paris Agreement, the ceiling of 2℃ average global temperature increase should not be exceeded to prevent the irreversible climate change, meaning the necessity of cutting GHG emissions from fossil fuels consumption (7, 8).

The need of changing the electricity and heat production technologies in power sector from fossil-based to greener alternatives leads to the necessity of the renewable energy sources development. According to forecasts of the International Energy Agency (IEA), the capacity of renewable power is expected to expand by 50% in the next five years, reducing total GHG emissions and decreasing the burden on the ozone layer. Solar PV plays the leading role in this projection, following by onshore wind power plants (9).

However, at this point the unstable production profile of renewable energy sources and its significant fluctuations, which is explained by variable weather conditions, becomes a problem. For the sake of reliable operation of power systems the production profile should be stable over time and be able to satisfy consumption needs, ensuring an instant demand-supply response. In the case of growing share of variable renewable energy, the implementation of supporting technologies is needed to balance the grid, smooth the fluctuations in power production and mitigate the variability challenge.

From this perspective, introduction of energy storage as a supporting technology for renewable energy sources becomes obvious and promising solution. The whole concept is based on the ability to store the excess energy, thermal or electrical, during the low demand period and release it later during the peak hours. Therefore, both grid performance optimization and greenhouse gas emissions reduction are achieved, following by undeniable economic benefits both for suppliers and consumers. Considering the significant growing of solar photovoltaics in the recent and upcoming years, storage of solar thermal energy becomes one of the crucial areas of investigation (10).

## 2.2 Thermal energy storage technologies

The operational principle of thermal energy storage (TES) is based on utilizing the excess heat into the storage medium, solid or liquid, and dispatching it by demand. Accordingly, complete cycle includes three steps: charge, storage and discharge. Thermal energy can be absorbed directly by the heat transfer fluid, which serves as a storage medium, or transmitted between separate substances from one to another during charging and discharging steps. In these circumstances, high storage capacity, good thermal conductivity, reversibility and stability of the storage material are becoming the main requirements while designing a thermal energy storage system (11).

Three major types of TES technologies known and used nowadays include sensible, latent and thermochemical heat storage. A comprehensive overview of these mechanisms is presented at Figure 1 (12).

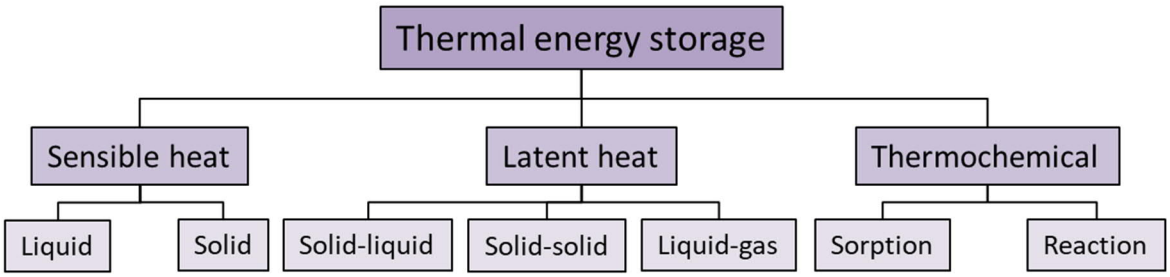


Figure 1. Classification of thermal energy storage mechanism (12)

### 2.2.1 Sensible heat storage

The operating principle of sensible heat storage is based on increasing or decreasing the temperature of the storage medium, which can be either in solid or liquid state. Specific heat capacity and density of the material are the main factors that define the efficiency. The relationship between the amount of heat stored, specific heat of the storage medium, the change of temperature and the mass of material is described by the formula (13):

$$Q = \int_{T_i}^{T_f} mC_p dT \sim mC_{ap}(T_f - T_i) \quad (1)$$

where $Q$ – quantity of heat stored (J), $T_i$ – initial temperature (°C), $T_f$ – final temperature (°C), $m$ – mass of heat storage medium (g), $C_p$ – specific heat (J/g K), $C_{ap}$ – average specific heat between $T_i$ and $T_f$ (J/g K).

The heat is absorbed by storage medium via the mechanisms of heat transfer (convection, conduction, radiation) and released while discharging the storage by the same way. Typical examples of materials used for sensible heat storage include water, rocks, and molten salts. For solar heating systems, water in plastic, fibreglass or glass-lined steel containers remains most commonly used storage medium because of its low cost and high specific heat (13). Yet, it requires a large volume of the thermal materials and thermal insulation to prevent heat losses to the environment.

### 2.2.2 Thermochemical storage

Thermochemical storage allows storing the thermal energy through reversible chemical reactions or sorption process. The advantages of this technology include high storage densities and minor thermal losses, making thermochemical energy storage attractive for long-term heat storage purposes. In terms of performance efficiency, thermochemical method usually outperforms physical ones (latent and sensible heat storage), but there is a challenge of finding suitable reversible chemical reaction. For example, water adsorption, carbonation reaction, ammonia decomposition, metal oxidation reactions and sulfur cycles were studied for this application (11). However, this technology is still immature and needs further research and development to provide a better stability and repeatability of the storage (5).

Generally thermochemical storage technology is based on utilizing the endothermic reaction to store the heat and then extracting it through reversible exothermic process. In other words, supplied heat is used to break the chemical bonds of the substance and split it into the components. The energy stored in chemical bonds has no losses regardless of the length of the storage period. Yet, the charged system needs to be protected from for example humidity in case of water adsorption during the storage time. Dehydration reaction of magnesium hydroxide into magnesium oxide is an example of reaction used for thermochemical energy storage (where $\Delta_R H$ – the supplied quantity of heat) (12):

$$Mg(OH)_2 + \Delta_R H \leftrightarrow MgO + H_2O \quad (2)$$

The sorption systems are also used for thermochemical energy storage and include adsorption on solid materials or absorption on liquids. The operating principle is based on binding the molecules of substance in gaseous or liquid state on the inner surface of a porous material. Charging step takes place during desorption, when adsorbed components are removed from the surface, and discharging happens when the heat is released during adsorption process. Zeolites and silica gels are the most common adsorbents (11).

### 2.2.3 Latent heat storage

Latent heat storage technology relies on phase transition process from one state of matter to another, usually between solid and liquid, although solid-solid and liquid-gas transitions are also possible. The storage medium in this case is called phase change material (PCM). The overall process of latent heat storage is shown in Figure 2. In the most common case of solid-liquid phase transition, the thermal energy is absorbed by the system during melting process and released when the material crystallizes, performing charging and discharging within PCM's phase change temperature range (11).

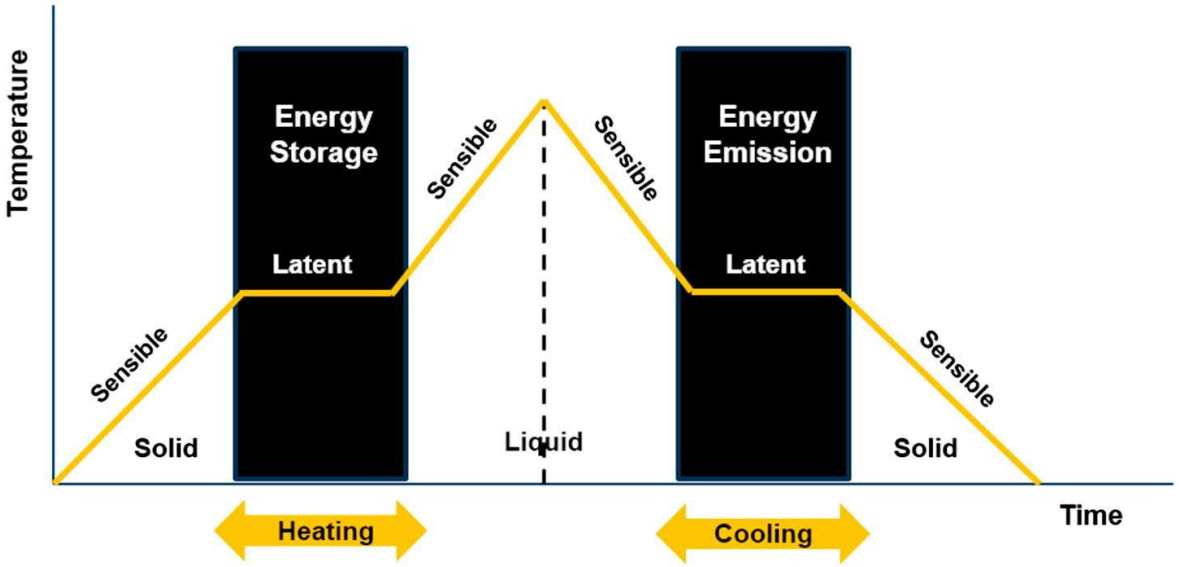


Figure 2. Schematic diagram of energy storage and phase change transition of PCM (1)

The temperature difference between melting and crystallization, alongside with storage temperature in case of long-term TES, defines the operating temperature range of latent heat storage system, while its efficiency to a significant extent depends on PCM's storage

capacity. The amount of thermal energy that can be stored in the system is defined by the formula (14):

$$Q = m(C_{p,s}(T_m - T_s) + \Delta H_m + C_{p,l}(T_l - T_m)) \quad (3)$$

Where $Q$ – stored energy, $m$ – mass of phase change material, $C_{p,l}$ and $C_{p,s}$ – average specific heats in the liquid and solid phases, respectively, $\Delta H_m$ – enthalpy of melting, $T_m$ – melting temperature of PCM, $T_s$ and $T_l$ – temperature of PCM in solid and liquid phases, respectively.

A large number of various substances have the ability to perform the phase transition with a certain heat of fusion within wide temperature range. However, to be applicable as PCMs for latent heat storage, those materials are required to exhibit certain physical, chemical and thermodynamic properties, which will be discussed in Section 2.3.

In comparison with other thermal energy storage technologies, latent heat storage appears to be the optimal in terms of efficiency and technology development, especially for long-term purposes. It provides significantly higher volumetric energy density within a narrower temperature range than sensible heat storage, which makes latent heat storage compact and economically feasible. Low pressure change inside the system during solid–liquid phase change transformation and absence of necessity to have a proper insulation in case of long-term storage with supercooled PCMs, also leads to savings in construction cost (14).

On the other hand, latent heat storage overcomes thermochemical storage systems in terms of simplicity, better development and wider implementation of technology. There are still numerous problems needed to be solved at the research and development stage of thermochemical storage, such as complexity and long-term reversibility of reactions, safety regulations and large investment costs (15).

## 2.3 Phase change materials for thermal energy storage

### 2.3.1 Overview

A wide range of materials have been studied for latent heat storage applications, but only few of them are suitable for commercialization. While choosing the appropriate substance as PCM, the main things to be considered are phase change temperatures within desired operating range, high heat capacity and thermal conductivity, safety and stability of the material, as well as its availability and low cost.

The desired properties of PCM for TES also include:

- minor volume change during phase transition;
- congruent melting;
- high nucleation rate;
- appropriate crystallization rate;
- reversible and repeatable melting-freezing cycle;
- non-corrosiveness and compatibility with constructing materials.

The classification of phase change materials can be considered from different points of view. Based on the phase transition temperature range from -20 to 200 °C, it can be divided into four groups of low, medium-low, medium and high temperature PCMs with specific

applications, presented in Figure 3. Another widely accepted classification divides PCMs into organic, inorganic, and eutectic substances, depending on the material nature, as it can be seen from Figure 4.

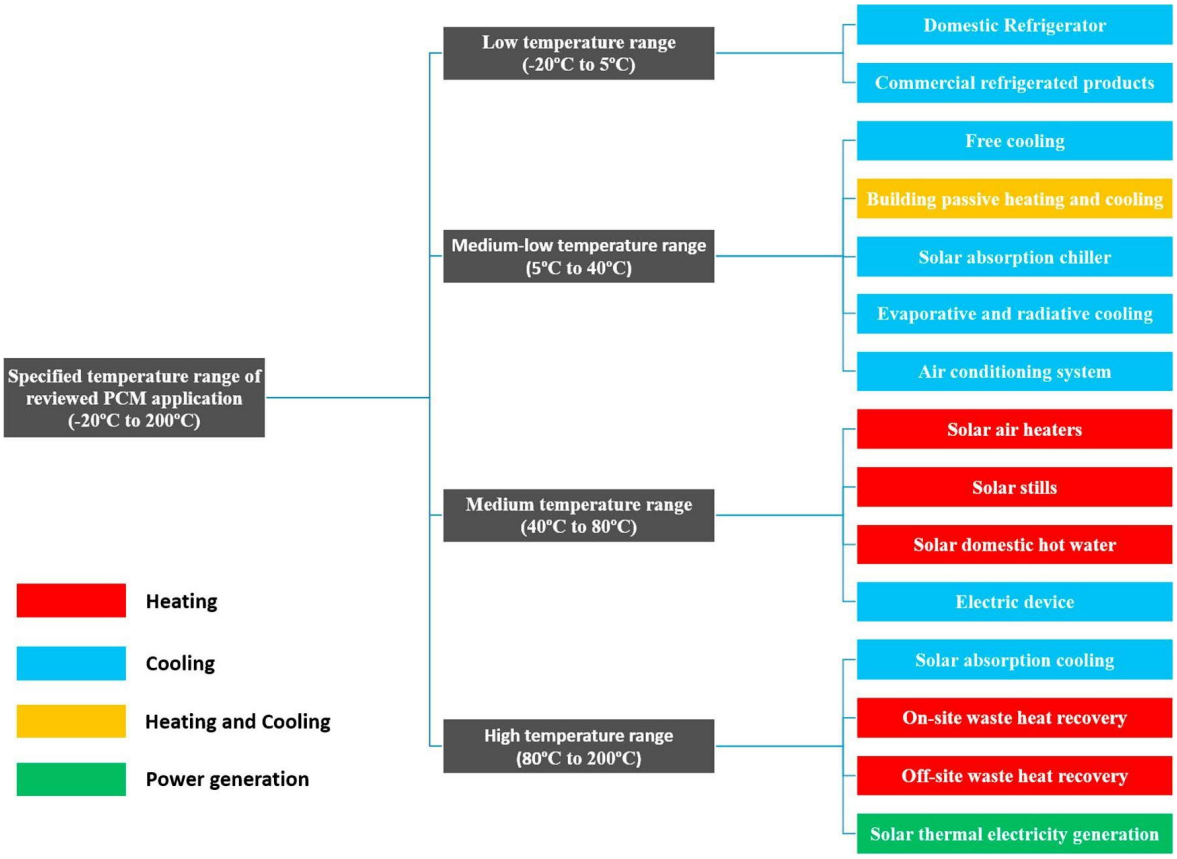


Figure 3. Classification of PCMs by operating temperatures and applications (1)

Inorganic compounds are mostly used in high-temperature storage applications. They usually do not experience significant melting enthalpy degradation over cycling (16). Inorganic PCMs can be further classified to two main groups: salt hydrates and metal alloys. Salt hydrates are crystalline solid material consist of inorganic salts and water molecules in their structure and can be described by general formula $AB{\cdot}nH_2O$. During the process of dehydration, the solid-liquid phase transition occurs, and the substance decomposes into either lower hydrate or anhydrous salt and water when it reaches the melting point. Salt hydrates have been extensively studied as PCMs for thermal energy storage applications due to their high energy density, decent thermal conductivity and economical profitability. However, such features as incongruent melting, phase separation and supercooling because of low nucleation rate may become a serious obstacle for industrial application of salt hydrates as PCMs. The other category, metallics, includes metals with low melting point and metal alloys. Regardless of low heat of fusion per unit weight, these substances are advantageous for thermal energy storage due to high thermal conductivity and heat of fusion per unit volume. Metallics demonstrate high thermal reliability and repeatability of thermal cycles and can potentially meet demands of large capacity power plants, if their cost and weight limitations are considered (16, 17).

Organic phase change materials are generally characterized by congruent melting and repeatable phase transition without segregation, as well as minor supercooling. Organic

PCMs can be divided to paraffin and non-paraffin compounds (including fatty acids, esters, alcohols etc.) Paraffins are saturated hydrocarbons, described by formula $C_nH_{2n+2}$. They show large latent heat of fusion, which increases with chain length, variability of phase change temperatures and stability. The major problem is related to low thermal conductivity of paraffin compounds, which requires incorporation of conductive particles and thereto related losses of storage capacity. Fatty acids with formula $CH_3(CH_2)_{2n}$·COOH have higher heat of fusion than paraffins but their high cost is a drawback. Non-paraffin organic PCMs show variable properties, but their common and important for TES application features include high heat of fusion, low thermal conductivity and instability at high temperatures (16).

Eutectic material is a composition of several organic or inorganic substances with similar phase transition temperatures. Eutectic mixture is capable of congruent melting and freezing without segregation of its components. To obtain different melting and freezing points, the weight percentage of each substance in the mixture can be varied. Therefore, eutectic phase change materials represent a promising field of research for thermal energy storage.

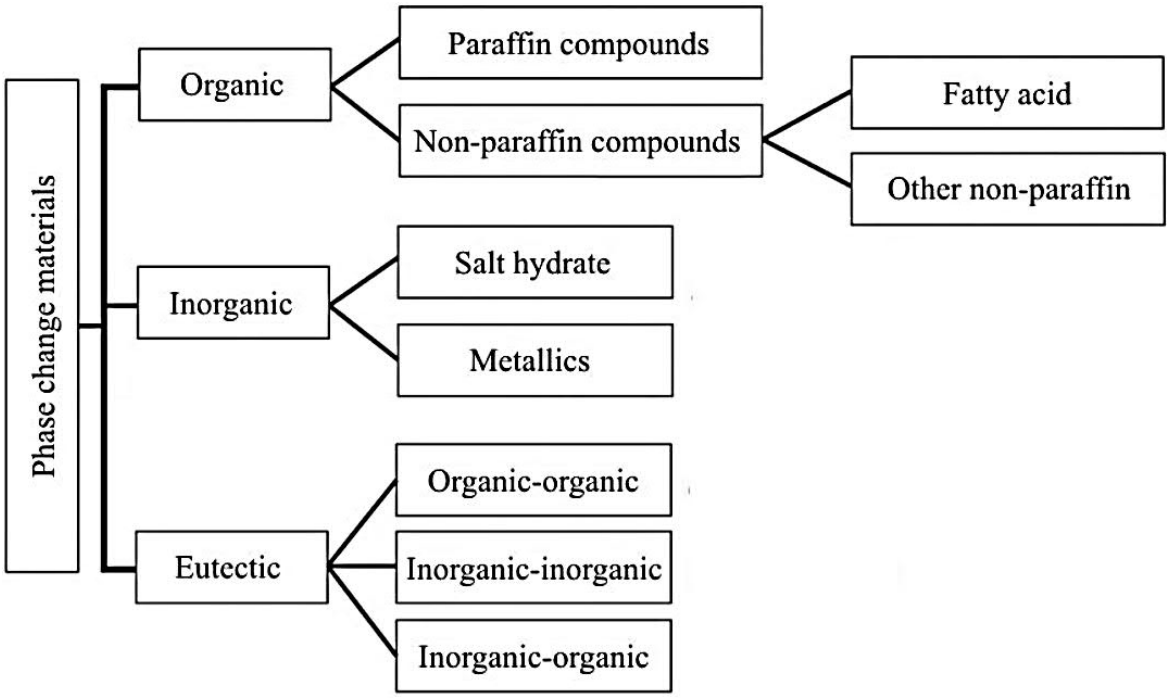


Figure 4. Classification of PCMs by substance (17)

### 2.3.2 Challenges and solutions

As described in Section 2.3.1, among the wide variety of substances used for thermal energy storage it is still a challenge to find an optimal phase change material for certain application, as every kind of material has its own drawbacks. Improving the properties of known PCMs and solving existing challenges requires a considerable amount research and development.

For instance, one of the major problems of PCMs application on a commercial scale is poor thermal conductivity of material, which negatively affects the charging and discharging times of the storage unit. To solve this problem, Mishra et. al. (18)

supplemented organic phase change material (phenol-water system) with $Al_2O_3$, $SiO_2$ and $TiO_2$ nano-inclusions, which resulted into large thermal conductivity enhancement. Addition of expanded graphite to PCM is also proven to significantly improve its thermal conductivity, as it was reported in (19, 20), showing the form-stability of PCMs/EG composites as well. Alternative techniques of heat transfer enhancement in PCM-based energy storage systems include inserting a metallic matrix, metal foams or impregnation of porous materials and using heat pipes (21).

Another issue, connected with latent heat energy storage, is the leakage of PCM when solid to liquid phase transition occurs. To overcome this challenge, encapsulation technique is used, meaning the coverage of PCM with suitable shell material. Thus, the coating holds liquid core and protects material from contamination, which is illustrated in Figure 5. Core-to-shell ratio is one of the critical parameters that define the encapsulated PCM's performance (22).

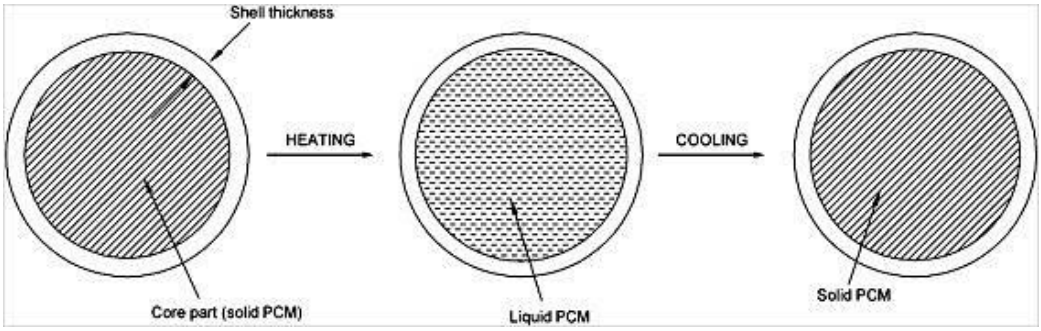


Figure 5. Structure and working principle of the encapsulated PCM (22)

Besides preventing the PCM from mixing with surrounding, microencapsulation can also improve cycling stability of the storage system and its thermal conductivity, in case the shell itself has higher thermal conductivity and acts as a heat transfer surface (21). While designing a thermal energy storage with encapsulated PCM, the selection of shell material needs careful attention. The desired properties of the coating material include compatibility with core material, non-reactivity, flexibility and stability. Preparation techniques of microencapsulated PCMs include chemical methods, based on various polymerization reactions, physic-chemical techniques like coacervation or sol-gel encapsulation and physical processes, such as spray-drying or electrostatic encapsulation (23).

The supercooling effect is usually seen as a problem for phase change materials for short-term TES. This phenomenon might involve a significant difference between melting and crystallization temperatures, which cannot be neglected. In other words, it happens when the temperature of PCM drops below the thermodynamic melting point before it starts to solidify. Thus, the heat storage cannot be discharged at desirable fusion temperature, preventing the withdrawal of thermal energy.

To mitigate the undesirable supercooling effect, the addition of nucleating materials is commonly used. The impurity provides a substrate on which the nuclei can form, acting as a catalyst for nucleation process and therefore decreasing the supercooling (24). For instance, the addition of silver nanoparticles to sodium acetate trihydrate showed the reduction of supercooling of PCM and consequently increased the latent heat recovery (25). Another effective nucleating agent has been proven to be aluminum nitride (26).

However, the supercooling effect is a controversial feature of phase change materials and can be turned into advantage under certain conditions. The positive effect of supercooling especially is recognized in long-term TES, for example when cold crystallizing PCMs are used for the purposes of long-term thermal energy storage (3, 5, 27), which will be discussed in Sections 2.4-2.5.

## 2.4 Short-term versus long-term thermal energy storage

The role of TES in advancing the renewable energy sources integration into thermal networks is defined by the gap between energy consumption and production. The mismatch may occur, for instance, because of the intermittent feature of solar energy production on a daily or yearly basis, difference in cost of the thermal energy over time or the distance between consumers and generation plants. As the thermal energy production must follow the load, these gaps result in decreasing the generation efficiency and increasing the risk of energy waste (28).

To avoid this, various thermal energy storage technologies are introduced, aiming to match the demand and supply on a time scale from hours and days up to several months. Short-term TES perform daily regulation of thermal energy distribution based on, for instance, peak-valley electricity rates of wind power plants. In this case, the specifically important technology parameters are operation controllability, low capital cost and high stability over many charge-discharge cycles. While batteries are widely used for short-term electrical energy storage, the thermal energy makes sense to conserve either by means of sensible heat storage systems, as the inevitable losses are negligible over a short period, or latent heat storage via phase change materials. For instance, salt hydrates are being investigated for the purpose of residential building heating (29).

Alternatively, long-term thermal energy storages are able to provide heat dispatch over months and seasons. For instance, in accordance with seasonal variations of solar radiation, seasonal TES are intended to charge during summertime, conserve thermal energy until winter and then discharge, providing consumers with heat depending on the load demand, which makes these technologies especially valuable in cold climate regions such as Nordic countries.

The main criteria for long-term thermal energy storage become low thermal losses over storage period, high energy density and especially the low investment cost, as because of low number of cycles and therefore low overall energy turnover, the energy capacity cost (EUR/kWh) increases (30). All three types of thermal energy storage technologies are feasible for long-term purposes. Sensible heat is commonly conserved underground in the form of aquifiers, using the groundwater as a storage medium, or boreholes, where the heat transfer fluid utilizes the underground heat. However, these technologies exhibit certain limitations due to complicated installation and high capital investment. Another common option is cavern thermal storage, in which heat or cold energy is stored in water reservoirs (underground storage tanks), integrated with the building heating system. The main challenges here are related to large storage volume and therefore high capital investments for excavation works and, most critical, proper thermal insulation to decrease continuous heat losses over long storage period (31).

Thermochemical storage, either based on sorption process or chemical reactions, is thoroughly suitable for long-term applications, as it provides with large storage densities

and insignificantly minor losses. However, the technology is still under development and appropriate system engineering solutions are needed to be found to implement it on a large scale. The alternative technology that is able to provide simultaneously high energy density and minimal losses is latent heat storage by virtue of supercooling phase change materials, which is researched extensively in recent years and introduced in the following section.

## 2.5 Supercooled PCMs for long-term TES

### 2.5.1 The phenomenon of supercooling

Supercooling effect occurs in phase change materials when instead of crystallizing and releasing the heat while reaching its equilibrium melting temperature the material remains in liquid metastable state. The molecular movement of substance gradually slows down when the temperature decrease, so the liquid behaves like glass or amorphous solid (2). The visual difference between liquid in its supercooled and solid states is shown in Figure 6 (2).

Figure 6. A supercooled liquid and its solid state (2)

The main reasons affecting the supercooling are connected to quick increase of material's viscosity during cooling or strong intermolecular interactions inside the substance (3), each of which hinders the rearrangement of molecules to form a crystal structure. It is also observed that the large enthalpy gap between liquid and solid states of phase change materials with high latent heat of fusion favors their severe supercooling (32).

Until the crystallization of supercooled liquid is induced either spontaneously or controllably, the latent heat is reserved inside of the phase change material without any losses. It means that the additional effort is required to release the heat, which is inefficient for short-term applications, but the ability to store thermal energy without losses for extended period of time makes the supercooling effect advantageous for long-term TES. For instance, the potential application of supercooled salt hydrates as PCMs was found reasonable in terms of amount of thermal energy that can be stored and released during crystallization (33, 34).

The degree of supercooling is an important characteristic, which should be taken into account while developing the novel PCMs. It represents the temperature gap between crystallization and melting points and can be described with an equation (2):

$$\Delta T_{sc} = T_m - T_c \quad (4)$$

Here $\Delta T_{sc}$ – supercooling degree, $T_m$ – melting temperature and $T_c$ – crystallization temperature. Because the crystallization heat release decreases alongside with freezing temperature drops, it is in researcher's interest to avoid too large supercooling degree. Therefore, it is important to keep the balance when it comes to the degree of supercooling to reach the most effective heat capacity of phase change material.

### 2.5.2 Cold crystallizing PCMs and their challenges

To release the heat stored inside supercooled phase change material by demand, the crystallization should be initiated. Possible mechanisms of triggering crystallization have been studied for supercooled sodium acetate trihydrate, a substance commonly used as PCM for various applications, and include supplying the seed crystal in the PCM's solution, using ultra-sonic sound as an activation mechanism and cooling with $CO_2$ to a low temperature (6).

Another promising activation mechanism that allows releasing the stored heat without using any additional substances is called cold-crystallization. In this process the heat impulse is used to increase the molecular movement inside PCM, which leads to relaxation to the crystal structure and release of the latent heat (27). The ability of certain materials to undergo cold-crystallization mainly originates from the high viscosity of supercooled liquids. Because of this, molecular mobility of the substance is redused and the rearrangement of crystal lattices is obstructed, which suppresses the crystallization of supercooled liquid PCM upon cooling. As the viscosity of the material decreases during reheating process, it improves the molecular mobility and induce crystal growth (35).

Supercooling behavior of various sugar alcohols have been extensively studied in recent years, and the ability of polyol-based PCMs to undergo cold-crystallization was revealed (3, 5, 32, 35). For instance, the upscaling of cold crystallizing PCM (erythritol dispersed in cross-linked sodium polyacrylate matrix) to the bulk storage of 160 g have been performed by Turunen et al. (27) and its supercooling and crystallization characteristics have been analyzed. The working principle of storage system is presented in Figure 7.

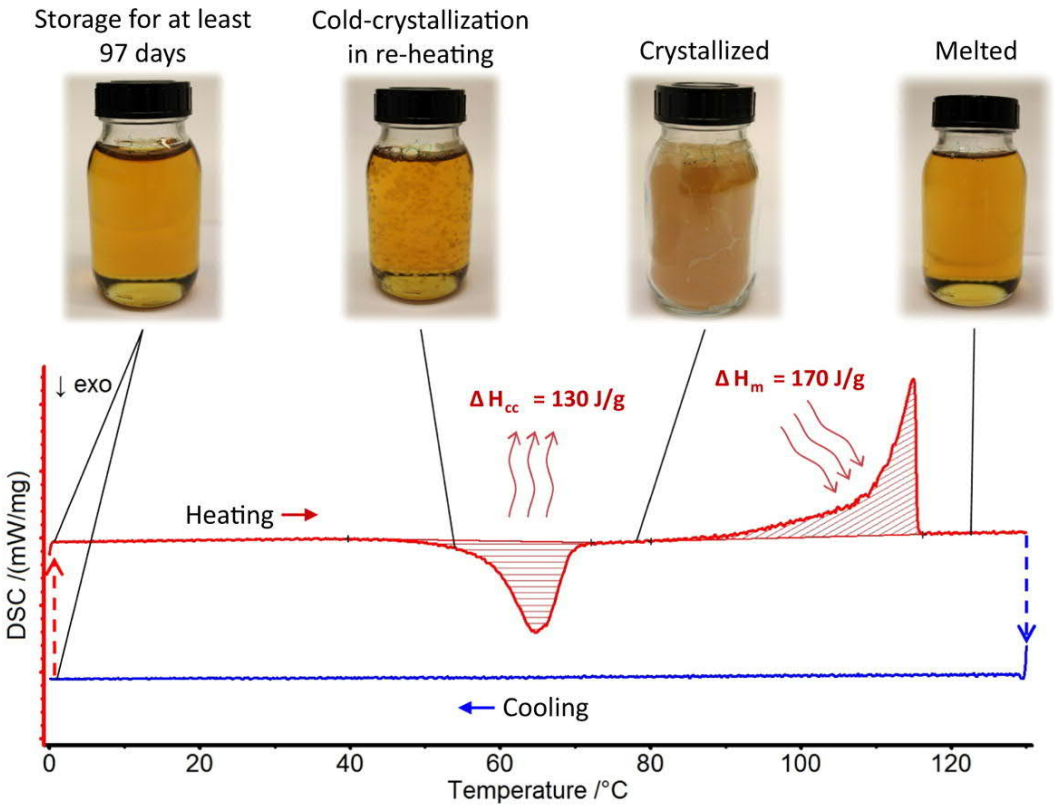


Figure 7. Heat storage in cold-crystallized PCM (27)

As it can be seen, charging of the storage happens by melting the material, while phase transition from solid to liquid takes place. After that the liquid is cooled down, and as the substance does not crystallize on cooling, which is essential for cold-crystallized PCM application, it remains in liquid state up to the glass transition point. In these conditions the supercooled PCM is able to store the heat without losses up to three months. To release the thermal energy the heat impulse is used, which is illustrated by crystallization peak on the DSC graph above. After that the solid crystallized PCM is ready for the next charging cycle.

Looking at it from the system level, a small part of the thermal energy is sacrificed for the possibility to conserve much bigger amount of it, so the storage system efficiency is defined by the difference. However, the degree of supercooling should be taken in consideration to avoid too high temperature of cold-crystallization. The closer crystallization temperature to the melting point, the larger triggering heat impulse is needed to start the crystallization of PCM, which would also reduce the overall storage system efficiency.

The key issues of supercooled PCMs application are related to poor stability of the material, which leads to thermal properties degradation over charge-discharge cycles. Corrosion of container walls while interacting with supercooled liquid, PCM's density change and phase segregation also requires attention and should be avoided (2). Therefore, the selection of suitable phase change material with certain thermophysical properties is important while developing a supercooled energy storage. The PCM should be stable, non-corrosive and require a high activation energy for the initiation of nucleation, which would obstruct the crystallization to occur spontaneously.

However, the main challenge is based on vulnerability of supercooled PCM to impurities, which act as nucleating agents and therefore can cause undesirable crystallization and spontaneous discharging of the storage system, as well as pressure changes or rough surface of container. While sample volume grows, the amount of impurities and probability of nucleation increase, therefore the upscaling tests are necessary while developing novel supercooled phase change materials (27).

## 2.6 Production of components

The novel phase change material that is being developed in this work consists of polyol-polymer mixture where erythritol, mannitol and polyvinyl alcohol are the main raw materials. Food-grade sugar alcohols and biocompatible polymer are intended to be safe and eco-friendly feedstock, however, to give a complete picture the whole production process of PCM's components needs to be assessed.

Erythritol global market is estimated to exceed 195 million USD in 2019 and due to increasing demand for healthy weight management products it is expected to grow at over 6.5% by 2026. Therefore optimization of erythritol production process remains an issue for industry players, making them invest in research and development (36).

Unlike to other polyols, erythritol production via chemical synthesis is not favored due to complicated reaction conditions involving high temperatures, nickel catalyst and low product yield, leading to higher costs. Instead, nowadays, industrial production of erythritol is based on biotechnological methods. Manufacturing is made by fermentation process using osmophilic yeasts such as Moniliella pollinis, Trichosporonoides megachiliensis, and recently also Yarrowia lipolytica. The substrate solution consists of glucose, which is gained from chemically and enzymatically hydrolyzed corn or wheat. The product is then recovered by separation from culture medium followed by ion exchange chromatography and crystallization. The formation of byproducts (other polyols such as mannitol, arabitol, ribitol, and glycerol) obstructs purification and decreases the yield of erythritol (37).

Taking into account socioeconomical issues, using crop species as a feedstock for starch-derived glucose is not preferable. Moreover, traditional production process reaches only around 40% (w/w) yields of glucose (which is a valuable compound itself) to erythritol conversion. Therefore, extensive research aiming at production cost reduction by finding alternative substrates are needed. For instance, Jovanović et. al. (38) developed a novel method to produce erythritol with the help of genetically modified mould fungus Trichoderma reesei using ordinary straw as a feedstock. An easily utilizable substrate is obtained by means of the alkaline organosolve pretreatment process of wheat straw, which is suitable for consecutive fungal growth. Successful manufacturing of erythritol from renewable, non-food substrate wheat straw shows promising perspective for large-scale production.

Alternative technology with a great industrial potential was proposed by Rakicka-Pustułka et. al. (39) and uses Yarrowia lipolytica yeast strain and glycerol as a carbon source. Being a by-product from biodiesel production plants or oleochemical facilities, residual glycerol becomes efficient, low-cost and renewable feedstock for erythritol production, showing above 50% product yield and expected production rate of 1075 MT/year. The sterilization is not required in biosynthesis of erythritol due to the medium's low pH. The process is

performed in non-aseptic conditions, lowering energy consumption and reducing the costs. Researchers also propose to use the remaining biomass as animal feed, making the new technology waste-free and economically viable.

In contrast to erythritol, commercial production of mannitol is based on chemical methods, in particular, hydrogenation of glucose and fructose containing syrup at high temperatures and in presence of nickel catalyst and hydrogen gas. The drawbacks of existing technology include low product yield, caused by the poor selectivity of the catalyst, making mannitol production dependent on the market demand of sorbitol, which is the main by-product. Complicated purification technology, expensive raw materials and high temperature conditions also affect production costs increase while having low production yields, which necessitates investigation of alternative production pathways for large-scale manufacturing (40).

A promising alternative to chemical method becomes biotechnological production of mannitol via fermentation using lactic acid bacteria and yeasts. Using food-grade microorganisms in manufacturing is especially beneficial for no need of complicated separation process. Related studies are mostly focused on increasing production yield of mannitol by fermentation pH control, fed-batch fermentation, using membrane cell-recycle bioreactor or genetically engineered microorganisms. These strategies are showing promising results of up to twice increase of mannitol production (40).

Being a water soluble, non-hazardous, non-toxic, and biodegradable polymer, polyvinyl alcohol (PVA) finds various applications from chemical to food industry. Increasing demand raises environmental concerns regarding PVA manufacturing, as this is a petroleum derived product. Instead of polymerization of the corresponding monomer PVA is prepared by hydrolysis of polyvinyl acetate, which is a product of vinyl acetate polymerization (41). The feedstock for vinyl acetate production includes ethylene and acetic acid, which are obtained from hydrocarbons and methane processing, respectively. The whole production pathway is depicted in Figure 8.

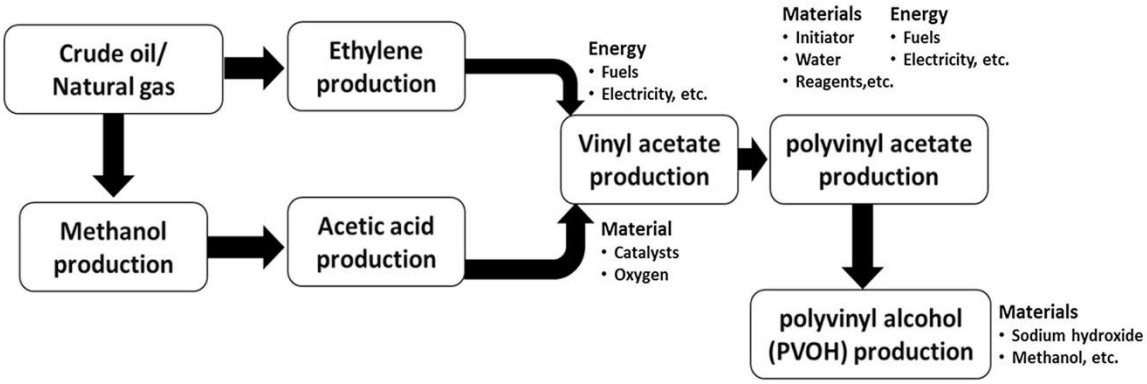


Figure 8. Polyvinyl alcohol production process (42)

It is logical to assume that the industrial manufacturing of a product of petrochemical origin will be associated with negative environmental impact. A comparative life cycle assessment of petroleum- and bio-based paper binder was performed by Anthony et. al. (42), including polyvinyl alcohol and distillers grains gum. The results show non-renewable energy consumption of 168 MJ/kg PVA and greenhouse gas emissions around

5.5 kg$CO_2$e/kg PVA. Vinyl acetate production contributes the largest fraction in both cases.

Summarizing the above, at the current step of technology development the large-scale industrial production of novel PCM's components would be aligned with some inevitable environmental burdens. For instance, polyvinyl alcohol is obtained from fossil feedstock alongside with other demanded chemicals, being a part of well-developed but emission intensive production chain. However, it takes relatively small (under 30%) fraction of the total material. Although the exact numbers concerning energy consumption and emissions from polyols production need investigation, the food crop derived glucose as a feedstock and relatively low product yields result to high production cost and negative effect to the environment. Nonetheless, due to increasing demand for the mentioned chemicals and developed production industry, the studies on improvement the manufacturing are being conducted, aiming to increase process efficiency and sustainability.

All major components of the novel phase change material are readily available on the market. The prices of erythritol, mannitol and polyvinyl alcohol are presented in Table 1.

Table 1. Market prices of PCM's compounds (43-45)

| **Compound** | **Market price, €/kg** |
|---|---|
| Erythritol | 13,00 |
| Mannitol | 21,38 |
| Polyvinyl alcohol | 27,65 |

From the economical point of view, the industrial production of novel phase change material is expected to be cost effective based on wide availability and reasonable market prices of its components. Erythritol, which takes major share of the PCM mixture, has the lowest market price. Moreover, the production process would not require complicated waste treatment. As mentioned, sugar alcohols are commonly used as sweeteners in food industry and therefore digestible, while polyvinyl alcohol is water-soluble and biodegradable, which makes the novel material to be non-persistent in the nature.

# 3 Research methodology

## 3.1 Research background

In this thesis, the mixtures of sugar alcohols and polymers are investigated from the perspective of long-term thermal energy storage. Shao, Wang et al. (35) performed the screening of single sugar alcohols and their binary eutectic mixtures in order to study their crystallization behavior. It was found that some of the mixtures were unable to crystallize upon cooling, but instead, the crystallization occurred during reheating process, which means the ability of the sugar alcohol mixtures to undergo cold crystallization. Puupponen and Seppälä (3) discovered polyol-polyacrylate mixture to be a promising supercooled PCM for long-term thermal energy storage. It reveals that dispersed in polymer matrix melt polyol supercools without crystallization and remains stable below its cold-crystallization temperature, also showing good sustainability over 100 charging-discharging cycles. Yazdani et al. (5) reported a tunable glass transition and cold crystallization of sugar alcohol dispersed in ionically crosslinked polyvinyl alcohol.

To this end, this thesis aims on developing sugar alcohol mixture with ability to cold crystallize, exploring the effect of the mixture ratio on its thermal behavior, and selecting the optimal composition as potential PCM for long-term thermal energy storage. The mixture of polyol sample with a polymer will be prepared to study the effect of polymer addition on the PCM's properties. The samples will be upscaled to the bulk size of 10 g to test their storage stability. In case of obtaining any promising results, the investigation of PCM's heat release stability over repeated melting and crystallization cycles will be performed, as well as the thermal stability tests.

### 3.1.1 Polyols as PCMs for TES

Sugar alcohols could be naturally found in various fruits and vegetables, or commercially manufactured. Polyols are widely used in production of polyurethane, as sugar replacers in the food industry and also in the pharmaceutical sector (46). However, in recent years polyols have received considerable attention as candidates for latent heat storage applications at low to medium temperatures. Their advantages include wide diversity of melting temperatures, high volumetric energy density, non-corrosiveness and high thermal stability (47). Most of the polyols are also undergoing stable and severe supercooling, which is a necessary requirement for long-term storage PCM.

Based on literature survey and results obtained during summer traineeship, the mixture of erythritol and mannitol was chosen as potential PCM, as it has a tendency to severely supercool. It is characterized by high phase change thermal energy storage capacity due to enthalpy of melting in the limits 310 – 340 J/g and enthalpy of cold crystallization around 160 – 200 J/g, depending on the mixture composition. The combination of mentioned features makes these sugar alcohols to be promising components of potential PCM for long-term thermal energy storage.

### 3.1.2 Improving PCM's properties with polymers

Using polymers as supportive materials for organic PCMs have been found to be reasonable in order to maintain the solid appearance of the developed composite material. It prevents the leakage of liquid PCM from its container (shape-stabilization), eliminates large volume fluctuations during phase change, as well as improves thermal properties of

material (48-50). For instance, Chen, Jiang et al. (51) proposed the novel erythritol-polyaniline form-stable PCM, which demonstrated good thermal stability over 100 melting and cooling cycles. Moreover, it was discovered that adding this particular polymer leads to significant suppressing of supercooling degree of polyol and increasing its solidification enthalpy.

Therefore, the addition of polymers can improve PCMs` properties in many aspects. However, the type of polymer has an effect on the desired properties. For instance, in the work conducted by Chen, Jiang et al. (51) addition of polyaniline polymer mitigated the supercooling property of polyol, while in case of long-term TES based on cold crystallization conducted by Puupponen and Seppälä (3) addition of polyacrylate polymer increased the degree of supercooling. Therefore, the right choice of polymer becomes essential. Turunen, Yazdani et al. (4) discovered one promising erythritol-PAANa composition showing stable supercooling and large latent heat of potential PCM. Another examined additive, that demonstrated improving properties as a supportive material, is polyvinyl alcohol. Besides of high latent heat of melting and cold-crystallization, the novel erythritol-PVA composition showed form-stability, preventing the leakage of the PCM in liquid phase (5).

### 3.1.3 Related studies

This thesis is built upon previously conducted research at Aalto University on erythritol-based phase change materials supplemented with various polymers. Puupponen and Seppälä (3) proposed the novel PCM-polymer mixture composed of erythritol dispersed in a cross-linked sodium polyacrylate (PAANa) matrix, which was further scaled up to a bulk size of 160 g (27), while Yazdani et al. used ionic citrate cross-linked matrices of polyvinyl alcohol (PVA) (5). The research is under the umbrella of Heatstock Project.

The Heatstock Project has showed the ability of specific polymers to eliminate the undesired crystallization of PCM during cooling, allowing the material to vitrify and stay in the supercooled state until the heat release is initiated by heat impulse (so called cold crystallization). This is explained by strong intermolecular interactions (ion-dipole forces or hydrogen bonds) between polyol and polymer. As a result, the phase change material is capable of stable and controllable charging and discharging.

However, those polyol-polymer mixtures were prepared using different methods. Polyol-PAANa samples were prepared by polymerizing the neutralized acrylic acid in aqueous polyol solution. Firstly NaOH was added to the polyol dissolved in deionized water. Then the mixture of monomer (acrylic acid) and cross-linking agent (ethylene glycol dimethacrylate) was slowly added to the basic solution at 60 °C. To initiate the polymerization reaction, potassium persulphate was added into a well-mixed monomer-polyol solution. Consequently, polymerization begun forming cross-linked polyol-PAANa gel. Finally, the samples was kept in the oven to vaporize the water (3).

By contrast to this, the preparation method of polyol-PVA mixtures does not include polymerization reaction. Ready-made polyvinyl alcohol was dissolved in distilled water at 70 °C, leading to the formation of homogenous hydrogel. Then it was mixed with polyol aqueous solution. Finally, sodium citrate dehydrate salt was added to the mixture for ionic cross-linking of the system. All the components were added under continuous mixing at

the temperature around 70 °C, and the complete formation of samples took around 2–3 hours. After that the samples were first dehydrated and then melted in the oven (5).

Both materials demonstrate stable supercooling, high heat storage capacity and appropriate operating temperatures. Thermal properties of obtained polyol-polymer mixtures are presented in Table 2, taking in consideration the varying composition of samples, scan rate and PCM to polymer ratio (5, 27).

Table 2. Thermal properties of ERY-PAANa and ERY-PVA mixtures

| PCM composition | Scan rate | $T_g$, °C | $T_{cc}$, °C | $\Delta H_{cc}$, J/g | $T_m$, °C | $\Delta H_m$, J/g |
|---|---|---|---|---|---|---|
| ERY-PAANa | 0.5 K/min | -18–-6 | 48–59 | -109–-128 | 106–108 | 138–173 |
| ERY-PVA | 5 K/min | -33.7–-28.5 | 10.1–28.6 | -133–-157 | 105.4–114.6 | 218.5–263.1 |

The melting temperature of both samples is similar. However, ERY-PAANa phase change material has slightly lower heat release due to lower melting enthalpy and possibly higher content of non-freezing fraction of the PCM caused by stronger intermolecular interactions from the polymer (5). The long-term storage stability in a bulk size (160 g) of ERY-PAANa has been studied, showing reliable performance up to 3 months under the storage temperature 0–5 °C (27). However, using hazardous chemicals and polymerization reaction for material preparation may make the potential production process of PCM more complicated and expensive comparing to its alternative.

PCM consisting of ERY-PVA mixture can provide high thermal capacity and a simpler fabrication process. The components used in the material preparation are safe and inexpensive, including food-grade erythritol and trisodium citrate as well as biocompatible polyvinyl alcohol. Moreover, addition of PVA gives PCM form-stability and leakage-preventive properties (5). There were no upscaling and storage stability testing of this PCM so far, but judging by glass transition and cold crystallization points, the potential storage temperature of PCM is expected to be between -15–0 °C, which means the extra energy need not only for discharging impulse but also for cooling to maintain the storage conditions. Therefore, the composition needs to be further tuned and adjusted by the salt and polymer concentration for a higher storage temperature.

This work analyses PVA as a supplementing polymer for novel PCM mixture because of its preparation simplicity, promising effect on material's properties and lacking of long-term storage performance tests in a bulk storage, which needs to be investigated.

## 3.2 Research questions and objectives

The aim of this research work is to develop a suitable polymer-polyol mixture for long term thermal energy storage applications, the working principle of which will be based on cold crystallization. The novel PCM should have proper thermal properties, i.e. be able to store the heat at appropriate temperatures and be stable over numerous charging/discharging cycles. Therefore, research questions are set to be: does the polyol mixture have a potential as PCM for long-term thermal energy storage, how can its properties be improved with polymer addition and what is the storage and cycling stability

of polyol-based PCMs? In order to accomplish an objective, several tasks should be performed:

- to prepare the mixtures of polyols of different ratios;
- to study the crystallization behavior of samples via DSC analysis;
- to choose the mixture with an optimal composition;
- to explore the effect of polymer addition on the properties of material;
- to confirm the composition of potential PCM for its long-term performance and cycling stability.

The expected result is to obtain a PCM with certain thermal properties, which include:

- high enthalpies of melting and cold-crystallization, which allows larger heat storage capacity;
- increasing the glass transition temperature so that the storage temperature can be at higher degrees, which leads to lower the energy consumption for storing the supercooled material;
- reasonable supercooling degree to ensure proper difference between charging and discharging heat impulses;
- good thermal stability over at least 50 melting-freezing cycles;
- ability not to crystallize spontaneously for up to a month.

## 3.3 Preparation method

Previous researches on sugar alcohols as potential PCMs are focused mostly on single substances. However, this thesis utilizes the binary mixture as potential stable cold-crystallized PCM for long-term heat storage. The effect of mixture ratio on its phase change behavior is studied. Mixtures of erythritol and mannitol, e.g. mass percentages 85/15, 80/20, 75/25 and 70/30 respectively, are prepared and tested.

Samples were prepared by mixing two sugar alcohol components at the required mass ratios, weighted on an analytical balance. The mixture was then thoroughly grinded in an agate mortar and heated in an oven above 120 °C for 2 hours to ensure a uniform mixing. Finally, the samples were cooled to room temperature and grinded prior to analysis.

Polyol mixtures combined with polyvinyl alcohol are prepared with PCM fractions of 85%, 80%, 75% and 70% with crosslinking 5% and 2% sodium citrate by adding homogeneous solutions of the components under vigorous mixing at 70–80 ℃, according to the method described by Yazdani et al. (5). The ready-made PCM-PVA mixtures were then dried in an oven at 70 ℃ for 1 day and melted at 120 ℃. These compositions may be adjusted by changing the concentration of salt and polymer in case of very high stability, which in return may prevent desired phase change behavior.

## 3.4 Analysis methods

Thermal analysis was performed by means of differential scanning calorimetry (DSC). The equipment used to analyze PCM's phase change behavior was Netzsch DSC204F1 Phoenix DSC. Measurement program to determine melting, cold-crystallization and glass transition properties included four consecutive heating-cooling cycles in a dynamic temperature range from -55 ℃ to 140 ℃. The scan rate either 5 K/min or 0.5 K/min was constant for heating and cooling. Similar program was used to determine specific heat

capacity of samples. For testing the cycling stability of PCM, two programs were used. The first one included 50 melting-cooling cycles in temperature range 20–140 ℃ with 5 K/min scan rate. The second program included 11 cycles within the same temperature range, heating rate 0.5 K/min and cooling rate 5 K/min. The sample was prepared by placing 10–20 mg of sample in aluminum crucible with a lid, each composition was measured twice. Phase change temperatures were determined by onset values and latent heat of fusion was calculated using the area under the peak. $T_g$ was defined by the end of glass transition region on heating. The thermogravimetric analysis (TGA) was performed on the simultaneous thermal analyzer Netzsch STA 449 F3 Jupiter in the temperature range from 20 ℃ to 450 ℃ under 10 K/min heating rate in nitrogen gas atmosphere.

# 4 Results and discussion

## 4.1 Preliminary results

Several mixtures of sugar alcohols were studied during summer traineeship, and some of the results are found useful for the current research. The thermal behavior of erythritol-mannitol mixtures depending on the ratio is presented below:

Table 3. Phase change temperatures and enthalpies of mixtures of erythritol (ERY) and mannitol (MAN) ($T_g$ is the end of glass transition region on heating, $T_{cc}$ and $T_m$ are the onset temperatures of phase transition, $\Delta H_{cc}$ and $\Delta H_m$ are the corresponding areas under DSC curve, scan rate 5 K/min)

| Sample composition | $T_g$, °C | $T_{cc}$, °C | $\Delta H_{cc}$, J/g | $T_m$, °C | $\Delta H_m$, J/g |
|---|---|---|---|---|---|
| ERY-90% + MAN-10% | -35.6±0.1 | 9.4±0.2 | -160.9±1.6 | 111.4±0.1 | 342.3±2.8 |
| ERY-80% + MAN-20% | -32.5±0.0 | 25.6±1.1 | -167.6±2.0 | 110.0±0.2 | 325.9±2.5 |
| ERY-70% + MAN-30% | -28.6±0.1 | 45.3±0.4 | -201.9±1.2 | 109.8±0.0 | 319.3±2 |
| ERY-60% + MAN-40% | -24.4±0.4 | 44.0±0.3 | -196.5±3.6 | 108.1±0.3 | 310.0±2.2 |

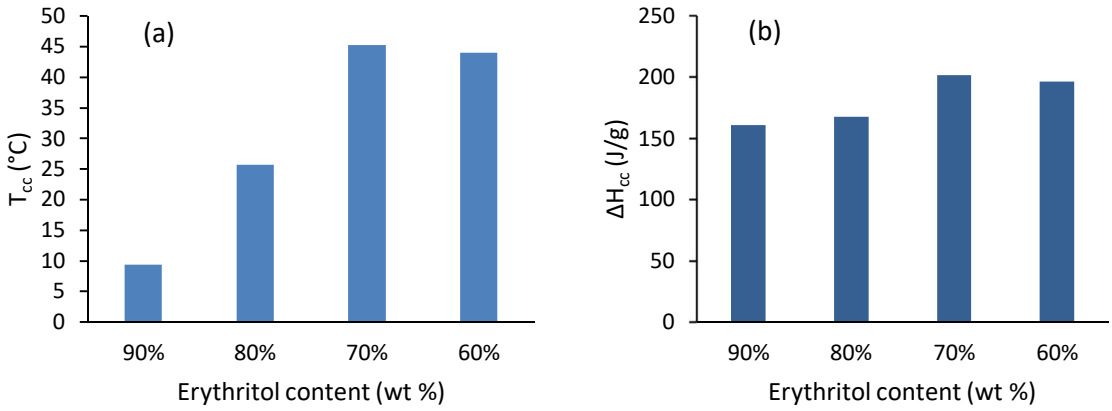


Figure 9. The effect of ERY-MAN mixture composition on $T_{cc}$ (a) and $\Delta H_{cc}$ (b)

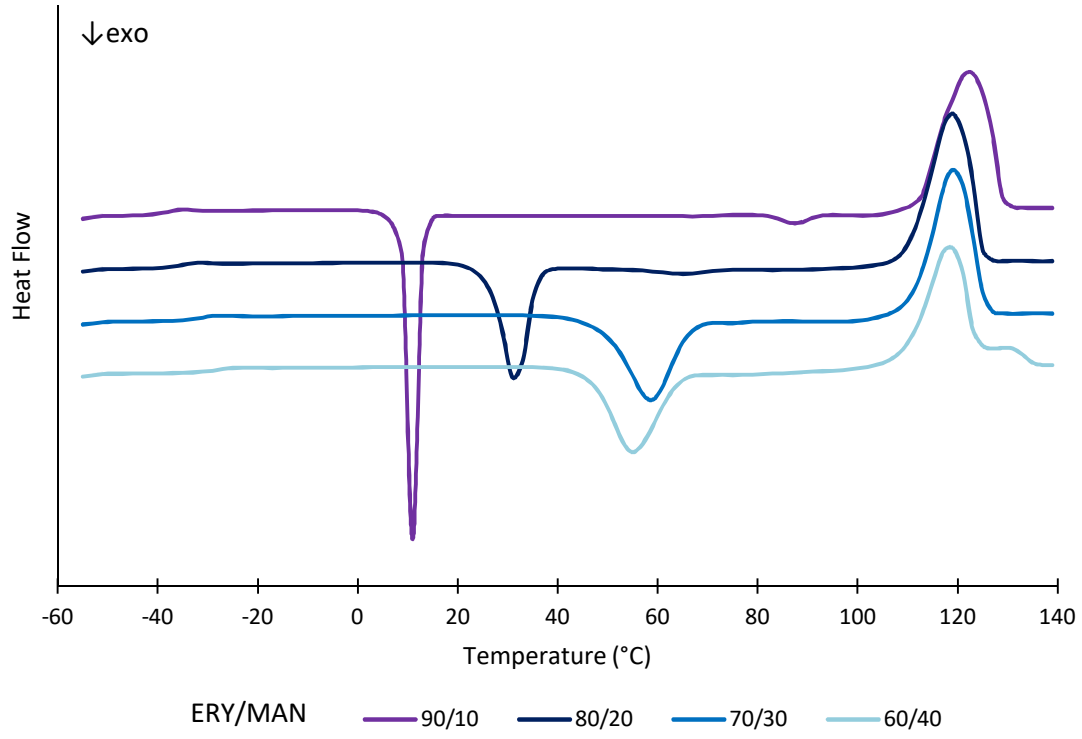


Figure 10. DSC curves of the ERY-MAN mixtures (scan rate 5 K/min, heating cycle)

The data presented in Table 3 are the average number of two repeated tests. The analysis was performed under scan rate 5 K/min. All the samples crystallize on heating and did not show any sign of crystallization on cooling. The results show clear increase of glass transition and decrease of melting temperatures, as well as amount of heat absorbed, with decreasing of erythritol content in the mixture. However, cold-crystallization temperature and heat release have a tendency to increase up to 45 °C and 202 J/g respectively until the erythritol content reaches 70%, but this trend does not sustain with its further decrease. Based on crystallization behavior, it's possible to assume that the optimal composition, which provides with highest heat release, lies around 70% of erythritol and 30% of mannitol. A set of subsequent tests within the narrower temperature range is performed in order to confirm the result.

The long-term heat storage performance and stability of polyol-polymer mixture was also examined by observing the samples of erythritol and polyvinyl alcohol (PVA) mixtures with rates 75/25 and 70/30. Samples were melted at 120°C for 4 hours and then kept in the fridge at 0°C for around one month. Throughout the storage period no significant change in the appearance which shows crystallization was observed. Further examination is needed to confirm that polyol-PVA mixture shows potential for long-term thermal energy storage. Another advantage of this polymer is that PVA gives form stability to PCM due to its ability to absorb polyol and keep the shape even after melting.

Figure 11. Erythritol-PVA samples immediately after melting (left images) and 4 weeks later (right images)

## 4.2 Polyol mixtures

Mixtures of erythritol and mannitol of mass ratio 85/15, 80/20, 75/25 and 70/30 respectively were prepared and tested in addition to experiments performed during previous research to compare results and narrow down the range of suitable compositions. Crystallization behavior of samples was studied via DSC analysis in temperature range from -55 °C to 140 °C and scan rate 5 and 0.5 K/min. Phase change temperatures and enthalpies of polyol mixtures are presented in Table 4. Here $T_g$ is the glass transition temperature, $T_{cc}$ and $T_m$ are the temperatures of phase transition, $\Delta H_{cc}$ and $\Delta H_m$ are the enthalpies of cold-crystallization and melting, respectively. Crystallization behavior of samples is depicted in Figure 12.

In comparison with preliminary results, there are slight variations in melting enthalpies for the same compositions, which may depend on the accuracy of measurement. However, the main trend of increasing $T_g$, $T_{cc}$ and $\Delta H_{cc}$ with the decrease of erythritol content in mixture is confirmed. All of the obtained results are relatively consistent with the ones reported in the literature for eutectic mixtures of erythritol and mannitol (with erythritol content 84% and 87%), where temperature of fusion is 113.10–114.05 °C and melting enthalpy 322.8–324.1 J/g (35, 52). The mixture of erythritol and mannitol is more promising for long-term TES purposes than e.g. galactitol and mannitol mixture, which demonstrated lower enthalpy of fusion (288.0 J/g) at higher temperature (153.1 °C) and cold-crystallizes only at high (over 10 K/min) heating rates (47).

Table 4. Phase change temperatures and enthalpies of erythritol (ERY)-mannitol (MAN) mixtures at scan rate 5 K/min

| Sample composition | $T_g$, °C | $T_{cc}$, °C | $\Delta H_{cc}$, J/g | $T_m$, °C | $\Delta H_m$, J/g |
|---|---|---|---|---|---|
| ERY-85% + MAN-15% | -35.3±0.4 | 13.7±0.8 | -159.5±0.6 | 109.8±0.4 | 319.8±0.5 |
| ERY-80% + MAN-20% | -33.1±0.1 | 23.2±1.7 | -167.8±4.4 | 109.4±0.2 | 315.2±4.5 |
| ERY-75% + MAN-25% | -30.9±0.9 | 36.6±4.2 | -190.2±4.1 | 110.4±1.1 | 318.6±0.8 |
| ERY-70% + MAN-30% | -29.9±0.6 | 43.4±1.5 | -203.7±3.5 | 110.1±0.8 | 310.9±2.2 |

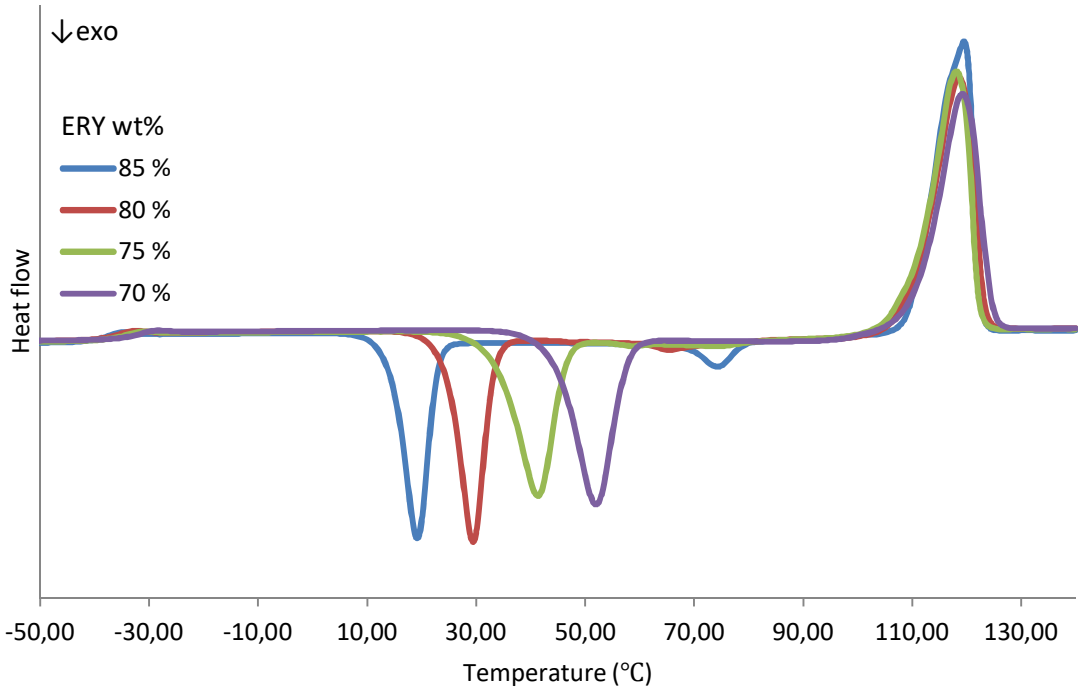


Figure 12. DSC curves of ERY-MAN mixtures of various ratios at scan rate 5 K/min

All the samples show no crystallization on cooling, but only on heating. Therefore, there are only heating curves presented in Figure 12. It proofs the ability of sample to undergo cold crystallization, which corresponds the goal of research. Compositions of ERY/MAN ratio 70/30 and 75/25 appear more promising due to stable crystallization behavior, which is demonstrated by absence of distortions on DSC curves in Figure 12, as well as higher $T_g$, $T_{cc}$ and $\Delta H_{cc}$. To define the optimal composition among them, DSC test with lower scan rate 0.5 K/min was performed. The results are presented in Figure 13 and Table 5.

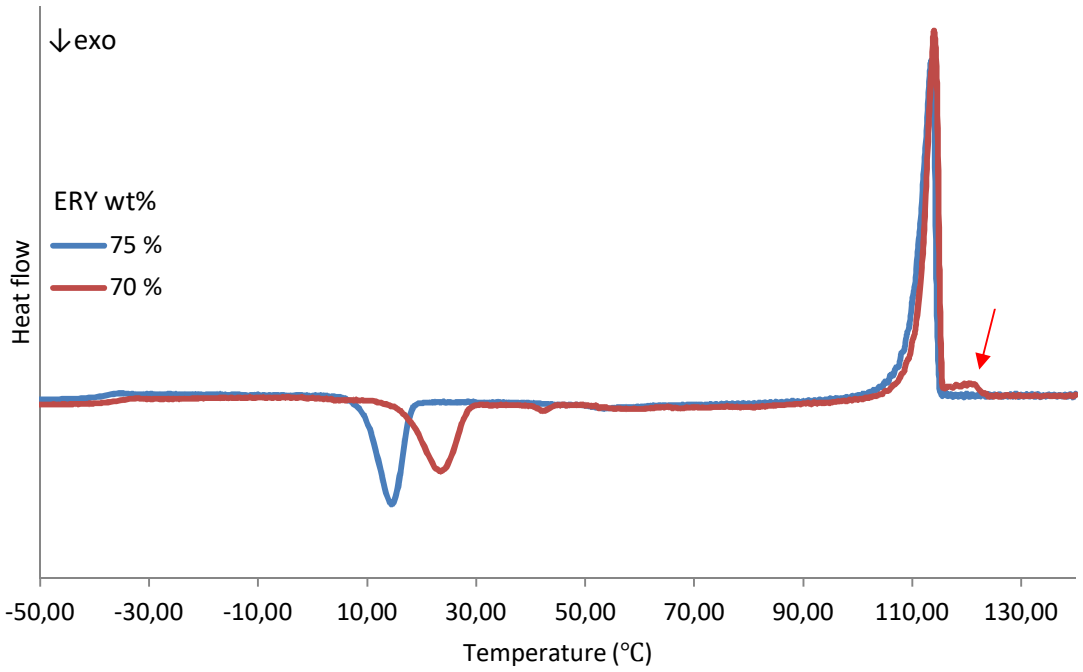


Figure 13. DSC curves of ERY-MAN mixtures of various ratios at scan rate 0.5 K/min

Table 5. Phase change temperatures and enthalpies of erythritol (ERY)-mannitol (MAN) mixtures at scan rate 0.5 K/min

| Sample composition | $T_g$, °C | $T_{cc}$, °C | $\Delta H_{cc}$, J/g | $T_m$, °C | $\Delta H_m$, J/g |
|---|---|---|---|---|---|
| ERY-75% + MAN-25% | -34.6 | 9.4 | -142.3 | 109.9 | 311.4 |
| ERY-70% + MAN-30% | -37.9 | 17 | -129.7 | 111 | 322.3 |

DSC analysis with the scan rate 0.5 K/min confirmed the stability of samples and its inability to crystallize on cooling even under very slow cooling rate. Decrease of glass transition and cold crystallization temperatures is expected by lower scan rate (53). As it can be seen from the graph, the sample with ERY/MAN content of 75/25 shows better crystallization curve with sharper peaks, no "shoulder" at melting peak and other distortions.

On the grounds of observations made, it can be concluded that the polyol mixture sample of 75% erythritol and 25% mannitol is the optimal composition between the others and deserves further investigation as a potential PCM.

## 4.3 PCM-PVA mixtures

To study the effect of polyvinyl alcohol addition to previously selected polyol mixture two sets of samples were prepared. The PCM content varies from 85% to 70%, including crosslinking 2% and 5% sodium citrate, as the concentration of crosslinking agent also effects on polyol-polymer mixture properties (5). The sample compositions are presented in Table 6.

Table 6. The compositions of prepared PCM-PVA mixtures in weight fraction (wt%)

| PCM | PVA | SC |
|---|---|---|
| 85 | 10 | 5 |
| 80 | 15 | |
| 75 | 20 | |
| 70 | 25 | |
| 85 | 13 | 2 |
| 80 | 18 | |
| 75 | 23 | |
| 70 | 28 | |

At first, DSC analysis under scan rate 5 K/min was performed to reveal an overall picture on the thermal behavior of samples and select the most promising ones for detailed testing. The results for the first set of samples with crosslinking 2% sodium citrate are presented in Figure 14.

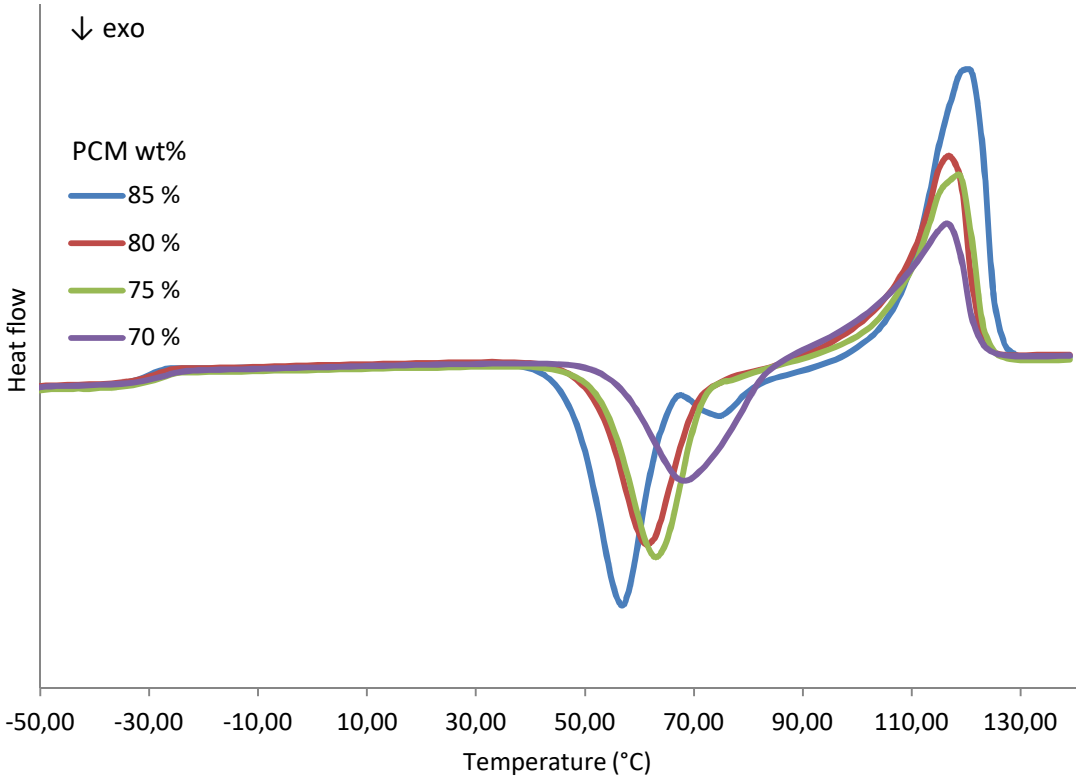


Figure 14. DCS curves of PCM-PVA mixtures with crosslinking 2% SC, scan rate 5 K/min

As all the tested samples do not crystallize on cooling, there are only heating curves presented in Figures 14–18. Out of first set, samples with the composition PCM-75/PVA-23/SC-2 and PCM-80/PVA-18/SC-2 seem to be more attractive for future testing, as they show high enough storage capacity and stable crystallization behavior without noticeable distortions at DCS curve.

The small distortions, such as secondary exothermic peaks and shoulders, are observed on the DSC curves of various samples in this research. According to Zeng et. al. (52), it may be explained by the polymorphic structure of both erythritol and mannitol. The overlapping of various components is reflected on DSC curves, considering also the variable composition of polyol mixture, none of which is eutectic. The polymorphism phenomenon occurs when a chemical compound exists in different crystalline forms which have various properties, and it is particularly important for e.g. pharmaceutical industry (54). However, it is not favorable in this research due to crystallization happening at different temperatures and therefore inability to extract all the heat from the storage at once. For this reason, the choice preference is made on those compositions showing the least DSC curve distortions.

However, to select the optimal composition the samples have been analyzed under lower scan rate 0.5 K/min, which let us to divide melting and crystallization peaks and evaluate clearer picture. The results are presented in Figure 15.

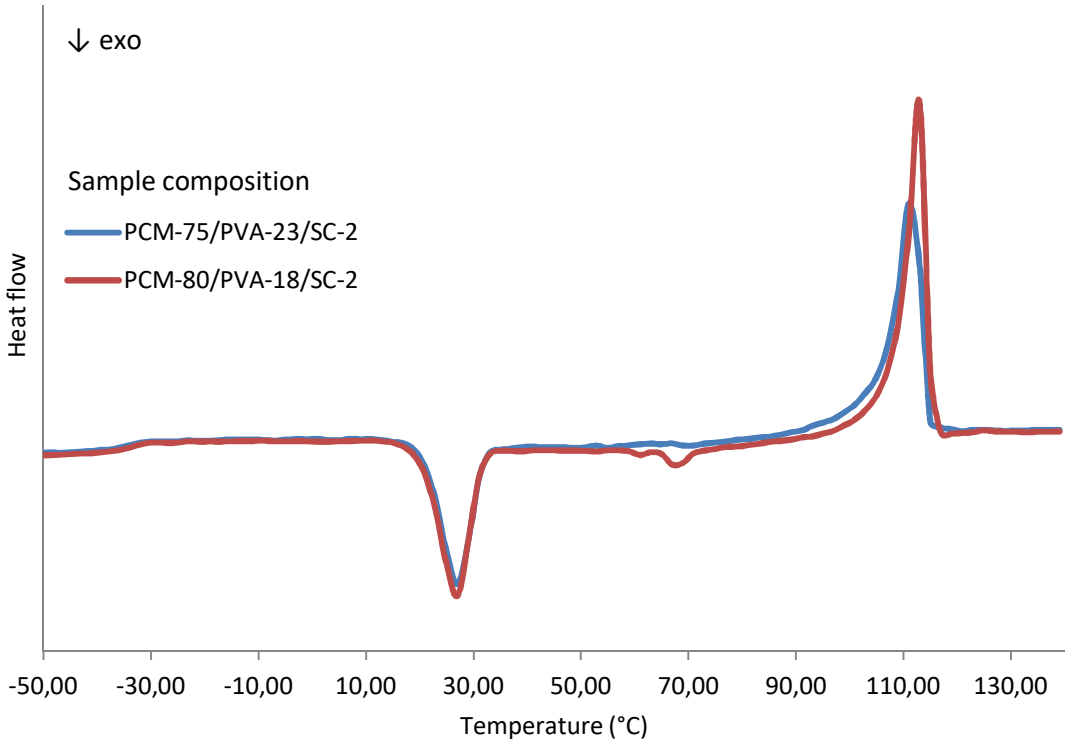


Figure 15. DCS curves of PCM-PVA mixtures with crosslinking 2% SC, scan rate 0.5 K/min

As it can be seen from the graph, the sample PCM-75/PVA-23/SC-2 shows better crystallization curve with no distortions, which makes it to be the best candidate as potential PCM out of the first set of samples.

The second set of samples with crosslinking 5% sodium citrate was analyzed in the same manner. The DSC curves with scan rates 5 and 0.5 K/min are presented in Figure 16 and 17 respectively. In the similar manner with the first set of samples, a pair of mixtures with the composition PCM-80/PVA-15/SC-5 and PCM-75/PVA-20/SC-5 showed high heat release together with consistent thermal behavior without secondary peaks and shoulders on DSC curves. These samples were selected for detailed study under slower scan rate. The sample PCM-80/PVA-15/SC-5 is defined as the best one between those with crosslinking 5% sodium citrate, as it demonstrates higher storage capacity, judging by larger peak areas at Figure 17.

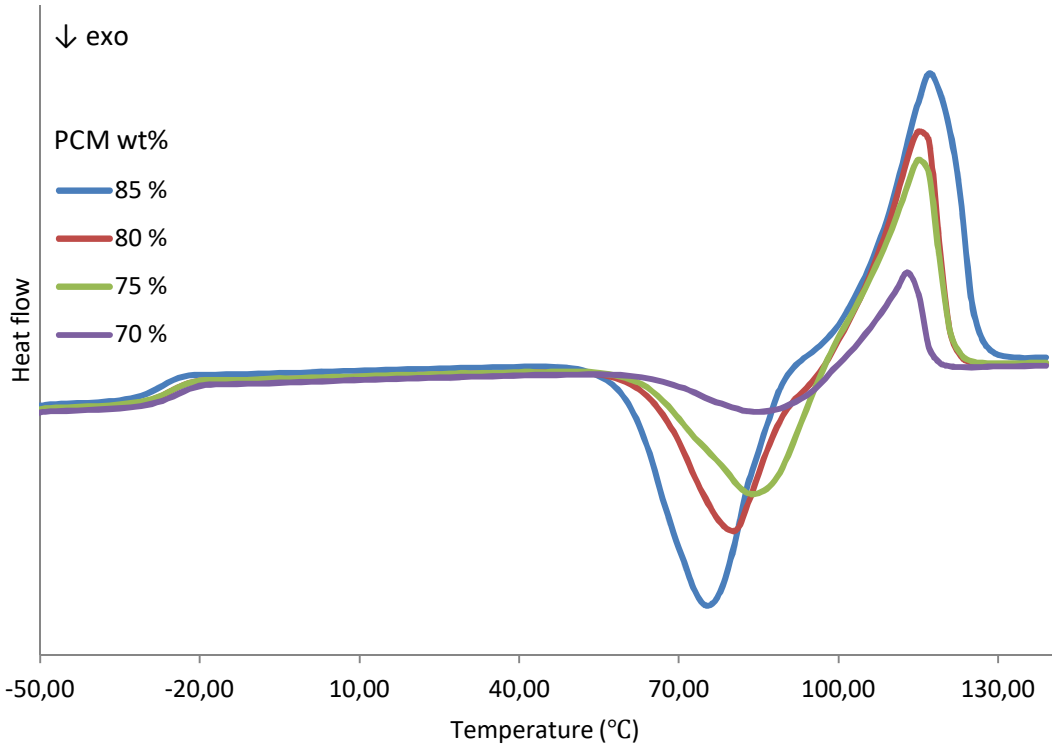


Figure 16. DCS curves of PCM-PVA mixtures with crosslinking 5% SC, scan rate 5 K/min

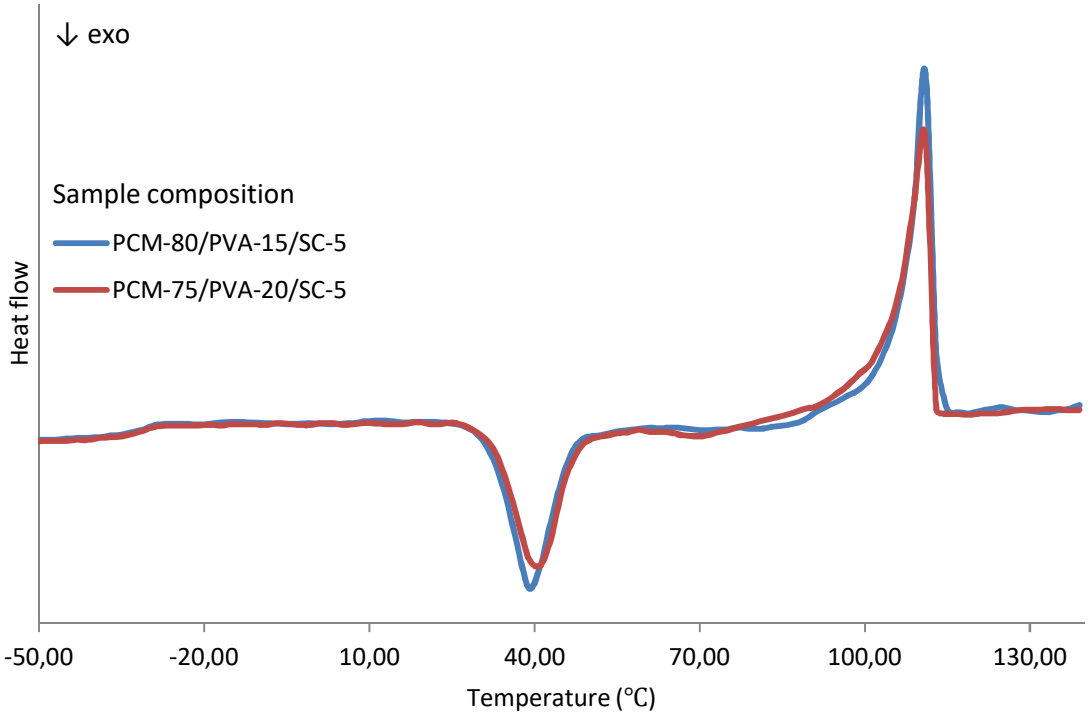


Figure 17. DCS curves of PCM-PVA mixtures with crosslinking 5% SC, scan rate 0.5 K/min

As a result, crystallization behavior of PCM-PVA mixtures of various ratios has been studied and samples PCM-80/PVA-15/SC-5 and PCM-75/PVA-23/SC-2 have been selected as the most promising candidates for using as phase change materials for long term thermal energy storage.

It should be also mentioned that those samples with higher concentration of sodium citrate (5%) stayed more stable in room temperature, while mixtures with 2% crosslinking started to crystallize immediately by for example touching or moving the samples. Therefore, for future upscaling and testing in a long storage period it makes more sense to focus on the composition PCM-80/PVA-15/SC-5. However, for both sets of samples the addition of PVA resulted in good shape stability, giving the PCM a consistent form in both melted and solid states. It occurs by virtue of super-absorbent properties of cross-linked polyvinyl alcohol matrices, which is able to swell in the polyol mixture and preserve the physical structure of PCM (5, 55).

## 4.4 Optimal compositions

In the experimental part of this work, a set of polyol and polymer-polyol mixtures have been prepared and tested to define the optimal compositions for potential long-term thermal energy storage applications. Thermal behavior of phase change materials has been studied via DSC analysis. The comparison of three best sample compositions is presented in Figure 18, showing their crystallization curves, while phase change temperatures and enthalpies of materials are given in Table 7.

Table 7. Phase change temperatures and enthalpies of polyol-polymer mixtures at scan rate 0.5 K/min

| Sample composition | $T_g$, °C | $T_{cc}$, °C | $\Delta H_{cc}$, J/g | $T_m$, °C | $\Delta H_m$, J/g |
|---|---|---|---|---|---|
| ERY-75/MAN-25 | -36.0±0.6 | 10.3±1.2 | -140.1±3.6 | 110.3±0.4 | 316.3±1.1 |
| PCM-80/PVA-15/SC-5 | -28.1±0.6 | 32.1±1.1 | -129.6±0.1 | 107.1±0.1 | 198.6±1.1 |
| PCM-75/PVA-23/SC-2 | -30.0±0.5 | 21.7±1.0 | -110.5±7.3 | 106.9±1.0 | 203.4±9.8 |

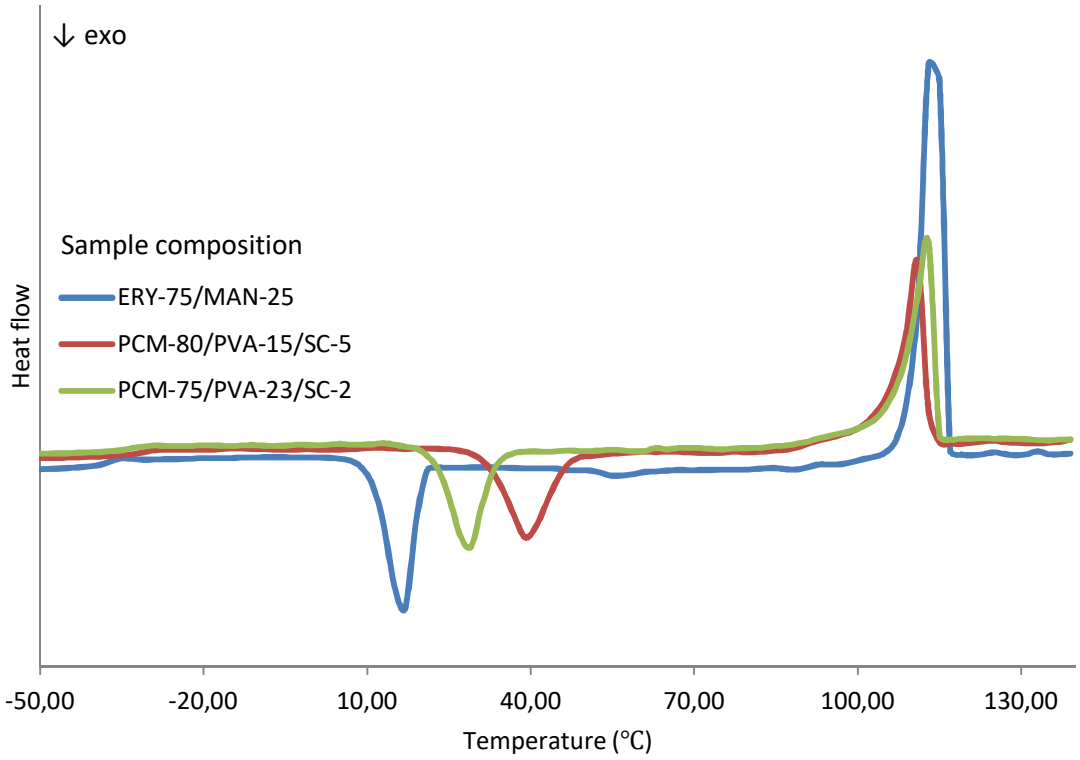


Figure 18. DCS curves of polyol-polymer mixtures, scan rate 0.5 K/min

The significant reduction of the melting enthalpy results from the lower content of phase change material in the mixture. Similar trend was observed, for instance, for erythritol-polyaniline PCM, which $\Delta H_m$ was about 260 J/g comparing with 345.3 J/g for pure erythritol (51). It also explains the decrease in cold-crystallization enthalpy, which would otherwise increase with higher $T_{cc}$.

Comparing the PCM composites with similar supporting material (PVA), using of binary polyol mixture instead of single erythritol results in lower melting heat. Che et. al. (56) reported melting enthalpy of 241.6 J/g for erythritol-PVA mixture ($m_{PCM} : m_{PVA} = 7 : 3$) and melting temperature 117.8 °C, while the results obtained by Yazdani et. al. (5) showed $\Delta H_m$ in the range 218.5–263.1 J/g and $T_m$ 106.3–112.8 °C depending on compounds ratio. The glass transition temperature at scan rate 5 K/min obtained in this research was -24.4 °C for a sample PCM-75/PVA-23/SC-2 and -21.8 °C for a sample PCM-80/PVA-15/SC-5, which is higher than the ones reported in the literature (-33.3 °C and -30.5 °C respectively)

for similar compositions with erythritol as PCM instead of binary mixture (5). Increase in glass transition temperature may be considered as advantage of using polyol mixture as PCM due to its effect on temperature of cold-crystallization, which leads to higher storage temperature.

All the selected samples show stable thermal behavior and high heat capacity, which makes them noteworthy as phase change materials for long-term thermal energy storage. However, addition of polymer into polyol mixture improves PCM's properties by increasing the possible storing temperature and making the material form-stable in melted state.

## 4.5 Specific heat capacity

Being a measure of energy needed to heat up the mass unit of material for 1 degree of temperature, specific heat capacity ($C_p$) is an important characteristic for sensible heat storage, as it directly affects the storage system efficiency. However, it is also important to consider for latent heat storage which working principle is based on cold crystallization, as the PCM needs to be heated up from storage temperature until it starts releasing the thermal energy. While melting heat defines the amount of energy needed to charge the storage, $C_p$ of supercooled material may be used to estimate the triggering heat impulse for cold-crystallization. The amount of energy required to initiate cold-crystallization ($\Delta H_{tr}$, J/g) is defined by the equation:

$$\Delta H_{tr} = m \cdot (T_{cc} - T_{st}) \cdot C_p \quad (5)$$

Here $m$ – mass of the PCM, $T_{cc}$ – cold-crystallization temperature, $T_{st}$ – storage temperature and $C_p$ – average specific heat capacity of supercooled PCM within ($T_{cc}$-$T_{st}$). As the heat capacity changes depending on temperature, the $C_p$ at mid-point between storage and cold crystallization temperature (which is meant by discharge) was used in calculations. Heat capacity of PCM in melted state is presented for comparison. Temperature and heat capacity data for three PCM compositions are shown in Table 8.

Table 8. Specific heat capacities of PCMs at various temperatures

| Sample composition | Storage | | Discharge | | Mid-point | | Melt | |
|---|---|---|---|---|---|---|---|---|
| | T, °C | $C_p$, J/(gK) | T, °C | $C_p$, J/(gK) | T, °C | $C_p$, J/(gK) | T, °C | $C_p$, J/(gK) |
| ERY-75/ MAN-25 | -20 | 2.299 | 10 | 2.459 | -5 | 2.346 | 130 | 2.842 |
| PCM-80/ PVA-15/ SC-5 | 0 | 2.217 | 32 | 2.389 | 16 | 2.308 | 130 | 2.766 |
| PCM-75/ PVA-23/ SC-2 | 0 | 2.090 | 22 | 2.240 | 11 | 2.170 | 130 | 2.682 |

The approximate energy impulse needed to discharge the storage is estimated based on Equation (5) presented above, and its values for each composition in comparison with the enthalpies of cold crystallization are shown in Table 9.

Table 9. Comparison of triggering heat impulse and energy release from the PCMs

| Sample composition | $\Delta H_{tr}$, J/g | $\Delta H_{cc}$, J/g | ($\Delta H_{cc}$– $\Delta H_{tr}$), J/g |
|---|---|---|---|
| ERY-75/MAN-25 | 70.38 | 140.1 | 69.72 |
| PCM-80/PVA-15/SC-5 | 73.86 | 129.6 | 55.74 |
| PCM-75/PVA-23/SC-2 | 49.28 | 110.5 | 61.22 |

Judging by the difference between the heat release from storage, which is defined by cold crystallization enthalpy, and the discharge heat impulse it is possible to conclude that latent heat storage based on polyol-polymer PCM is reasonable. However, the energy needed for discharge may also be partly obtained from excess heat depending on specific application conditions. The values of useful heat release do not vary significantly, so the conclusion about the best PCM composition should be made based on specific application, storage condition and the results of storage stability tests in bulk sample size, which will be presented further in this work.

## 4.6 Bulk storage tests

To assess the storage stability of PCM mixtures, the samples were upscaled to bulk size of 10 g, melted in the oven at 120°C to charge the storage and then placed in the fridge at 0°C. By visual changes in sample's appearance it was possible to observe the start of crystallization process, meaning discharge of the storage. The images of pure polyol mixture (ERY-75/MAN-25) and polyol-polymer mixtures (PCM-80/PVA-15/SC-5 and PCM-75/PVA-23/SC-2) in melted, supercooled and crystallized states during the storage period are presented below in Figures 19–21.

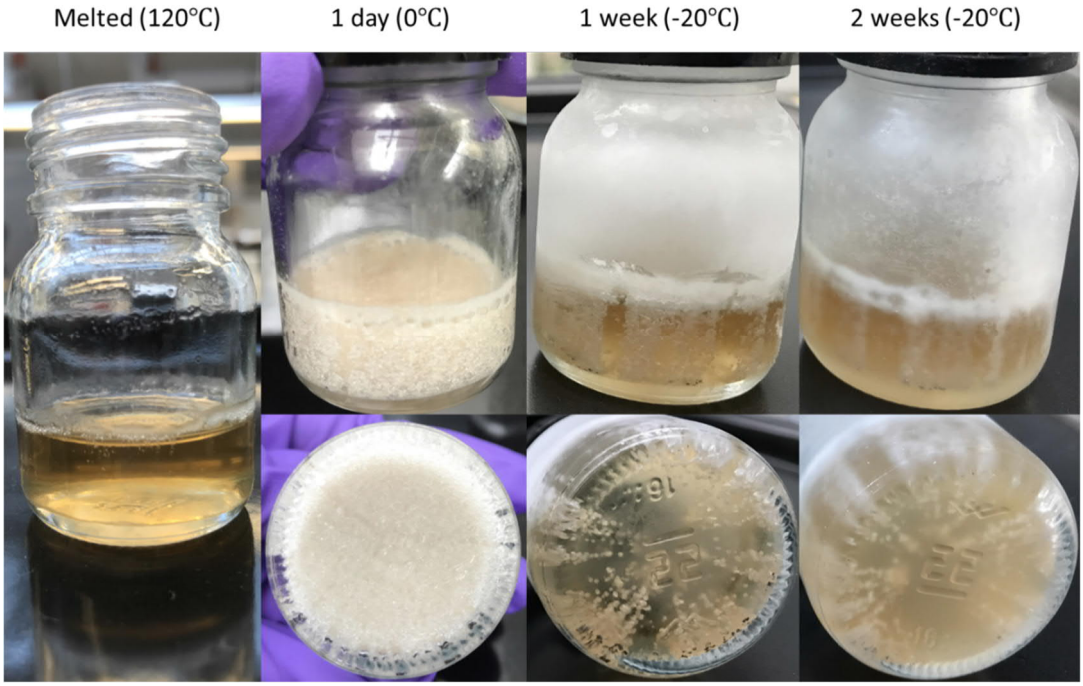


Figure 19. Images of pure polyol mixture sample (ERY-75/MAN-25) during the storage period

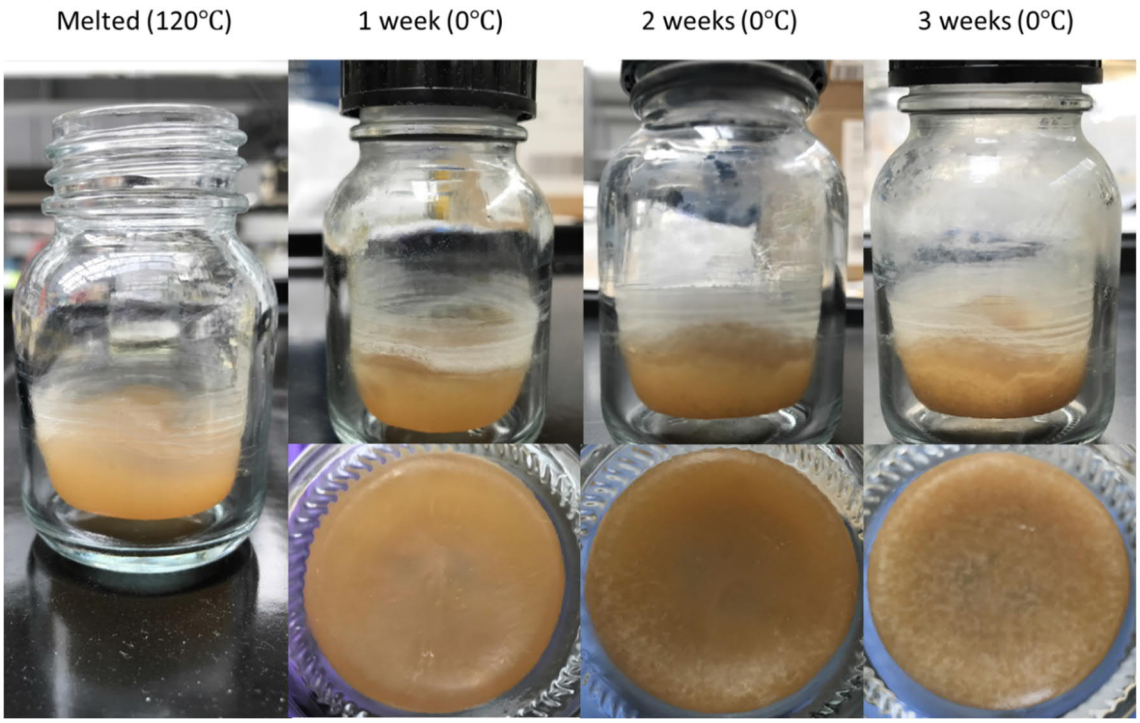


Figure 20. Images of polyol-polymer mixture sample (PCM-80/PVA-15/SC-5) during the storage period

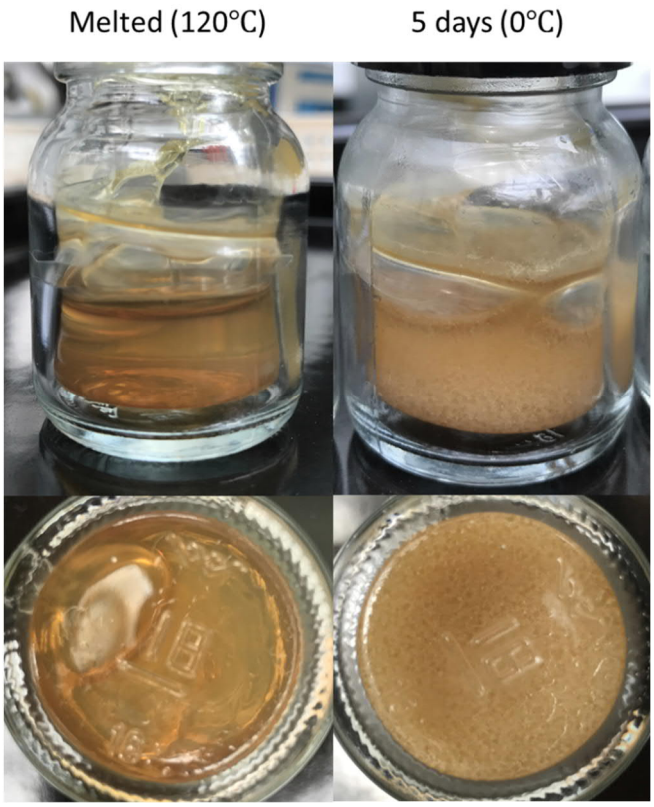


Figure 21. Images of polyol-polymer mixture sample (PCM-75/PVA-23/SC-2) during the storage period

The target storage temperature was set to 0°C, as it would allow minimizing the energy consumption for storage period of PCM. Bulk size tests show that pure polyol mixture without polymer addition is unable to keep up these conditions, as it completely crystallized already the next day. However, sample ERY-75/MAN-25 demonstrates good stability at -20°C. After 1 and 2 weeks of storage period there are few crystallization cores visible in Figure 19, but overall mass of the sample remains in supercooled liquid state.

Same polyol mixture improved with PVA addition shows noticeably better behavior. Sample with 5% crosslinking (PCM-80/PVA-15/SC-5) is able to be stored at 0°C up for 2 weeks, but afterwards the crystallization starts and proceeds. However, mixture with smaller concentration of crosslinking agent demonstrates lower stability: sample PCM-75/PVA-23/SC-2 shows clear signs of crystallization already after 5 days of storage. And thus, it may require lower storage temperature than zero degree.

Based on these results it is possible to conclude that polyol-polymer mixture with composition PCM-80/PVA-15/SC-5 has a potential for TES applications, although it would require the future research and development in terms of increasing the storage period and measuring heat release of bulk storage. Moreover, it is worth mentioning that addition of PVA to PCM mixture gives it shape stability, which is visible in pictures by difference of samples' appearance in melted state. This unique feature of polymer matrix would significantly improve the PCM's properties, as it prevents its leakage from container.

## 4.7 Cycling stability

The stability test over 50 DSC heating-cooling cycles was performed for the sample PCM-80/PVA-15/SC-5, as this composition is assumed to have the most beneficial properties as potential PCM for long-term thermal energy storage in industrial and domestic applications. The repeatability of the sample's phase change behavior is presented in Figure 22.

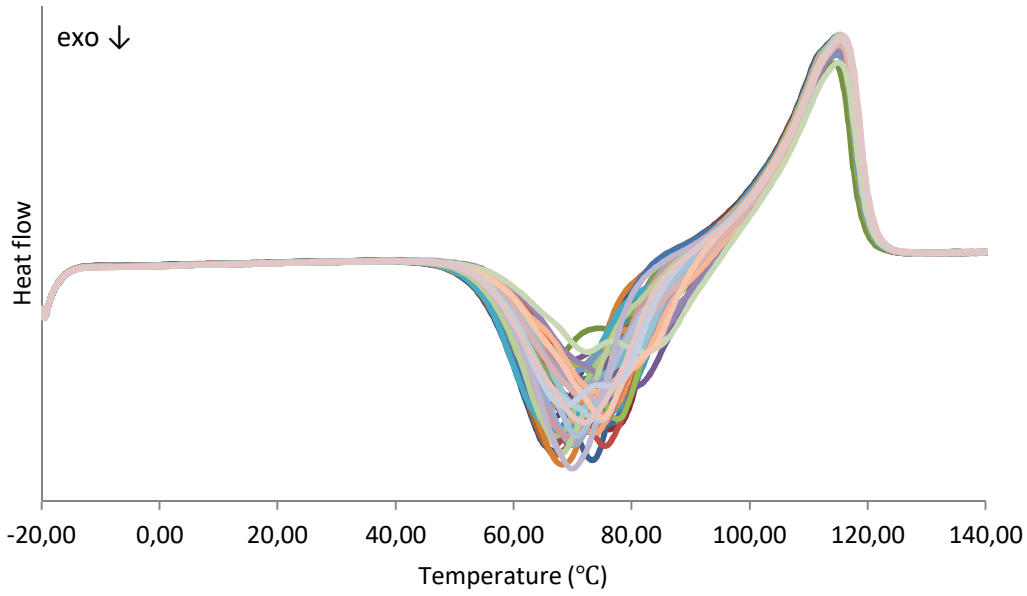


Figure 22. Repeatability of phase change behavior of PCM sample PCM-80/PVA-15/SC-5 over 50 DSC heating-cooling cycles, scan rate 5 K/min

The sample demonstrates good repeatability of melting, however, its crystallization behavior noticeably changes over cycling. This might be due to high scan rate (5 K/min) which lead to a closer occurrence of cold-crystallization and melting when the material does not find enough time to fully crystalize before melting starts. The pattern of crystallization peaks variety does not follow a specific trend. Cold crystallization temperatures of a sample at scan rate 5 K/min lie within a range 54.1–57.9°C. Incoherent manner of PCM's cooling behavior might be explained by incomplete crystallization of a sample at the tested scan rate, as the peaks merge into one another.

For the more accurate assessment of sample's thermal behavior, additional test was performed, including 11 consecutive cycles with heating rate 0.5 K/min and cooling rate 5 K/min. As the PCM crystallize on heating, only heating curves are presented in Figure 23.

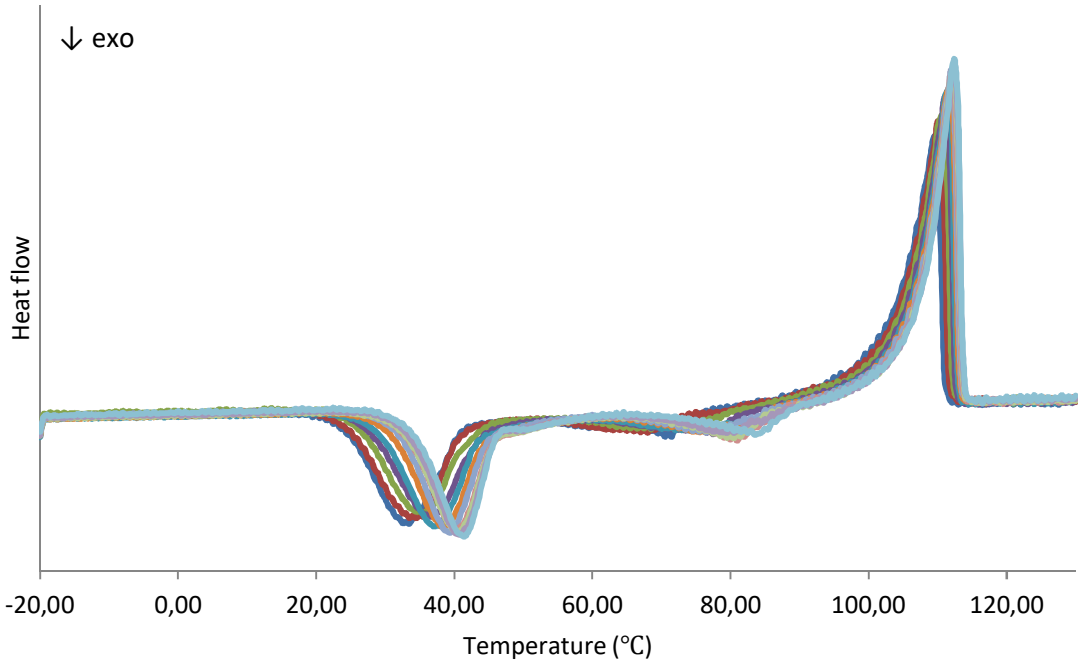


Figure 23. Repeatability of phase change behavior of PCM sample PCM-80/PVA-15/SC-5 over 11 DSC heating-cooling cycles, heating rate 0.5 K/min, cooling rate 5 K/min

The DSC graph shows consistent increase of cold-crystallization temperature over cycling from 24.2 °C to 33.8 °C and consequently, heat release increase from 120.8 J/g to 130.8 J/g, as the crystallization at higher degree leads to higher heat release. The melting behavior of the sample is more consistent, $T_m$ and $\Delta H_m$ insignificantly vary inside the limits 103.3–108.0 °C and 210.9–205.6 J/g respectively. Similar properties were observed by Che et. al., when the PCM composite consisting of erythritol, PVA and graphene has shown slight latent heat degradation of 1.2% after 10 thermal cycles (56). However, there are heating curve distortions of uncertain origin appear on the graph around 70–80 °C, which was not observed before, when heating and cooling rate were both 0.5 K/min.

As a consequence, the consistent melting behavior and rather small variations in crystallization behavior give a good characteristic to the novel PCM's cycling stability, although the clear trend to cold-crystallization temperature increase should be considered

as a challenge in future PCM's development, as it would require higher triggering heat impulse to discharge the storage.

## 4.8 Thermal stability

To analyze the thermal stability of PCM mixtures, the thermogravimetric analysis (TGA) was performed. Both samples, including pure polyol mixture without polymer addition and the target PCM-PVA mixture, were heated from the room temperature to 450 °C. The thermogravimetric profile of samples is presented at Figure 24.

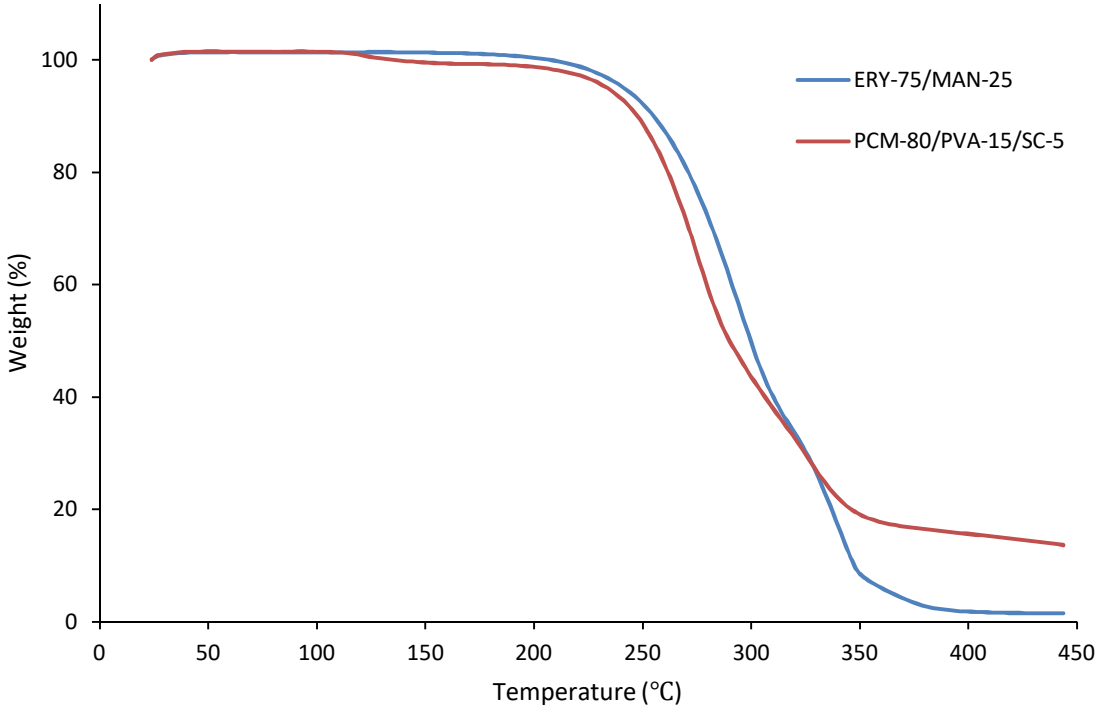


Figure 24. TGA profile of polyol mixture (ERY-75/MAN-25) and polyol-polymer mixture (PCM-80/PVA-15/SC-5) samples

Both materials demonstrate good thermal stability within operation temperature range (up to 150 °C). The weight loss starts around 230 °C, followed by complete thermal decomposition of PCM within 350–380 °C. The PVA-containing material shows slight weight increase in the end of the degradation process comparing to polyol mixture, which is explained by decomposition of polyene residues to carbon. Previously reported thermal decomposition of erythritol-PVA cold-crystallizing phase change material was observed within the narrower temperature range of 200–300 °C (5). Apparently, the degradation profile is affected by the more complicated PCM composition, which includes binary mixture instead of single polyol.

# 5 Conclusions

In this thesis the novel polyol-polymer mixture was developed for long-term thermal energy storage. Based on theoretical analysis, phase change materials for latent heat storage could be the optimal solution for cold climate regions to satisfy the heat demand in a sustainable way, collecting solar heat during summer, storing it for a few months and releasing by desire in wintertime. The analysis of related researches revealed that cold-crystallized polyol-polymer mixtures are showing promising results in this respect.

The studied composition includes erythritol and mannitol mixture as phase change material, dispersed in ionic cross-linked polyvinyl alcohol matrices. The raw materials are food grade and non-toxic chemicals. The PCM obtained by simple fabrication method has a unique ability to cold-crystallize on reheating, meaning that it is able to store heat in supercooled state and release it by demand through applying a heat impulse.

Wide range of samples of various ratios was studied to define the optimal composition with better properties, which appears to be a mixture of 75% erythritol and 25% mannitol, dispersed in 15% PVA with 5% crosslinking sodium citrate. Thermal behavior of sample was studied by means of differential scanning calorimetry, demonstrating high latent heat of melting (198 J/g) and crystallization (129 J/g). The feasibility of material is confirmed by significant difference between storage heat release and discharge heat impulse.

Bulk storage tests revealed that polyol-polymer mixture can be stored at 0 °C up to 2 weeks before the crystallization process starts, demonstrating high potential for large-scale applications. On the contrast with PCM based on pure polyol mixture, which storage temperature is around -20 °C, PCM-PVA mixture does not require significant amount of excess energy to keep up the storage temperature conditions. Besides that, polymer addition improves mechanical properties of PCM by making it form-stable, which would prevent its leakage from container in melted state.

According to cycling stability tests, the PCM has satisfactory repeatability, including stable and consistent melting over 50 heating and cooling cycles. Crystallization temperature has a clear tendency to increase, which should be considered for potential application. Thermal stability test has shown that the novel material is stable up to the highest operation temperature limit of 150 °C.

Overall, the research outcome of this thesis demonstrates sustainable way of long-term thermal energy storage by means of novel PCM based on polyol-polymer mixture. The material is especially advantageous in terms of shape stability and high heat capacity, although its relatively short storage period and change in crystallization properties over cycling need to be considered for further research and development.

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